GEOGRAPHIC DISTRIBUTION OF THE DITERPENES FROM THE MARINE BROWN ALGA *Dictyota* LAMOUROUX (DICTYOTALES, PHAEOPHYTA)

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ABSTRACT

The presence, abundance and diversity of **Dictyota** diterpene skeletons are correlated with the collection area of studied algae. It is shown that the geographic distribution of the diterpenes parallels the biogeography of the taxon, and that the highest variety of skeletons is found in the Indo-Pacific region, claimed to be the dipersion center of the genus. Our results corroborate O. R. Gottlieb's Theory of Micromolecular Evolution that states that invasion of new areas results in modification in the relative importance between the characteristic metabolic pathways of a given taxon.

Key words: Diterpenes, **Dictyota,** geographic distribution

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Financed by CAPES, CNPq and FINEP.

Nerítica, Pontal do Sul, PR, **2**(supl.):179-200, dezembro 1987

RESUMO

Distribuição geográfica dos diterpenos da alga parda Dictyota Lamouroux (Dictyotales, Phaeophyta).

A presença, abundância e diversidade dos vários grupos de esqueletos terpênicos em **Dictyota** são correlacionados com a região de coleta da alga. Observamos que a distribuição geográfica destes produtos coincidiu com a biogeografia do taxon, apresentando a maior variedade de esqueletos na região Indo-Pacífica, proposta como o centro de dispersão do gênero. Os resultados obtidos corroboram a Teoria da Evolução Micromolecular de O. R. Gottlieb, segundo a qual a invasão de novas áreas resulta numa modificação na importância relativa entre as vias metabólicas características do taxon.

Palavras chave: diterpenos, **Dictyota**, distribuição geográfica

INTRODUCTION

In 1809, Lamouroux described the genus **Dictyota** and included 23 species into it, PAPENFUSS (1977). Since then, several were transfered to other genera or were considered questionable species, and many other were added to the genus. Presently, problems to establish the separation limits between species and varieties still exist for a number of **Dictyota** representants, DAWSON (1950), OLIVEIRA FILHO (1977). It has been shown that the use of secondary metabolites may serve to determine some of these limits, TEIXEIRA (1985). Accordingly, in recent years, studies focused principally on diterpenes have contributed to a better knowledge of the taxonomic position of several **Dictyota** species, TEIXEIRA (1985), TEIXEIRA & KELECOM (1987).

Phytochemical studies have been undertaken on algae of the genus **Dictyota** resulting in the isolation of more than 80 diterpenes from at least 16 species collected all over the world. The lack of available information on representants from the South Atlantic Ocean was filled in by our recent work on **Dictyota cervicornis** Kützing, TEIXEIRA et al. (1986a, b). Such an amount of chemical data allowed us to try to establish correlations between geographic distribution of **Dictyota** species and structural variation of their associated diterpenes. It seems that these major secondary metabolites are directly related to herbivory control in Dictyotaceae, KELECOM & TEIXEIRA (1986). Indeed, parallel investigations on several algae and herbivorous mollusks have allowed to determine herbivores diets and to establish particular food chains, indicating specific predator-prey pairs. Thus, variations in the relative amounts of diterpene skeletal groups from algae collected in various oceans might be related to geographic variations in predation impact, KELECOM & TEIXEIRA (1986), TEIXEIRA (1985).

The genus **Dictyota** is found essentially in tropical and subtropica waters. It contains about 30 species and is considered to be originated from the Indo-Pacific region, CHAPMAN & CHAPMAN (1981), HENRIQUEZ (1982), from where it spread being now largely distributed in the Pacific, where it spread being now largely distributed in the Pacific, Indian and Atlantic Oceans and in the Mediterranean Sea, HENRIQUEZ (1982).

In this work, we wish to report on the geographic distribution and on the structural variations of the diterpenes found in **Dictyota** species. Phylogenetic speculations are made. Finally, it is proposed that the effectiveness to control herbivory of the major diterpene skeletons, and hence of the metabolic pathways leading to them, may be dependant of the region of the world.

METHODS

The diterpenes, isolated from **Dictyota** species and reported until June 1986, have been separated in three chemical groups (I, II and III) depending on their skeleton and following our previous biogenetic considerations on the first cyclization of the common geranyl-geraniol precursor, TEIXEIRA (1985), TEIXEIRA et al. (1985). Group I includes principally prenylated derivatives of knows sesquiterpene skeletons that derives from a first cyclization of the precursor between positions 1 and 10 or 1,10 an 1,11. Group II contains the diterpene skeletons resulting from cyclization of geranyl-geraniol between C-1 and C-11. Group III contains skeletons exclusively found in marine organisms. They derive from ring closure between C-2 and C-10 of geranylgeraniol, TEIXEIRA (1985), TEIXEIRA et al. (1985), TEIXEIRA & KELECOM (1987).

Dictyota species were separated following the collection area: Indo-Pacific, Atlantic and Mediterranean regions. In order to detect and to analyse possible correlations existing between the occurrences of diterpene skeletal classes and the algae collection areas, we calculated:

1º. the percentage of compounds from chemical groups I, II or III in each geographic region, relatively to the total of diterpenes known for that region, **i.e. the** occurrence (in %) of these three groups in the Indo-Pacific, Atlantic and Mediterranean regions;

2º. the percentage of compounds from chemical groups I, II or III in each geographic region, relatively to the total of diterpenes known for each chemical group, **i.e.** the diversity in compounds of each group as a function of the region; and

3º. the major skeleton in each area.

It must be emphasized that the phytochemical data published on **Dictyota prolificans,** KAZLAUSKAS et al. (1978), RAVI & WELLS (1982), have not been considered here, since our chemosystematic results, TEIXEIRA (1985), TEIXEIRA & KELECOM (1987) and independant botanic studies, ALLENDER & KRAFT (1983), transfered this species from the genus **Dictyota** to **Dilophus intermedius.** Similarly, the diterpenes isolated from an unidentified **Dictyota** species from the Sicilian coast, TRINGALI et al. (1984a, b, c, 1985), have not been included in agreement with our previous chemosystematic work, TEIXEIRA & KELECOM (1987) and also since a new taxonomical classification of studied algal material showed that this alga was in fact **Dilophus fasciola,** TRINGALI et al. (1986).

RESULTS

The list of chemically studied **Dictyota** species appears in Table 1. Diterpenes have been isolated from nine species collected in the Atlantic Ocean, one in the Mediterranean Sea and nine in the Indo-Pacific region, for a total of 16 different correctly identified species of the genus **Dictyota.**

On the whole, **Dictyota** species furnished 82 diterpenes of which 37% (30 structures) possess skeletons of group I, 39% (32 structures) of grupo II and 24% (20 structures) of group III (see Figure 1). Considering the three geographic regions, the following numbers were obtained. Algae from the Indo-Pacific region yielded 51 products (100%), of which 45% with skeletons of group I, 18% of group II and 37% of group III. Algae from the Atlantic Ocean, including the Caribean Sea, furnished 28 diterpenes (100%), 36% of which from group I, 61% from group II and only 3% (a single xeniane) from group III. Species from the Mediterranean Sea yielded 13 metabolites (100%), 38% belong to group I and 62% to group II (Figure 1).

Analysis of Figure 1 showed a clear decrease in the frequency of diterpenes from group III, going from the Indo-Pacific region to the Mediterranean Sea, and concomitant increase in the frequency of diterpenes from group II. On the contrary, the frequency of diterpenes from group I did not suffer significant variation, or at most a slight diminution, on going from the Indo-Pacific region (45%) to the Atlantic Ocean (36%) and Mediterranean Sea (38%).

In order to quantify such tendencies, the percentages of occurrence and diversity of diterpenes from each chemical group, in each geographic region, are presented in Figures 2, 3 and 4. In these figures, the 100% is the total of diterpenes of groups I, II and III respectively that have been isolated from Dictyota species. Hence, among the 30 diterpenes of group I (100%), 77% were obtained from algae collected in the Indo-Pacific, 33% from species of the Atlantic and 17% from the Mediterranean Sea (Figure 2). An evident decrease in the diversity of these diterpenes is thus observed going from the Pacific to the Atlantic and finally to the Mediterranean region. The 32 diterpenes of group II (100%) are distributed as such: Indo-Pacific 28%, Atlantic 53% and Mediterranean 25% (Figure 3). The diterpenes of this group are thus more characteristic of the Atlantic Ocean. It should be noted that all the diterpenes of group II that have been isolated from algae of the Mediterranean Sea belong to the dolabellane skeleton. Figure 4 represents the percentage of diterpenes from group III in the various considered areas. They clearly dominate in the Indo-Pacific region with 95% of the products of that group known for the genus.

Considering the most characteristic skeletons for each region (Figure 5), the following results were obtained: 55% of diterpenes isolated from algae of the Indo-Pacific region are prenylated guaianes (group I) and xenianes (group III); 61% of diterpenes from algae of the Atlantic Ocean are dolastanes and secodolastanes (group II); and 62% of secondary metabolites from the Mediterranean Sea are dolabellanes (group II).

The nine investigated species of **Dictyota** from the Indo-Pacific region (Table 1) furnished 51 of the 82 diterpenes (62%) and 14 (82%) of the 16 skeletons known for the genus. From the

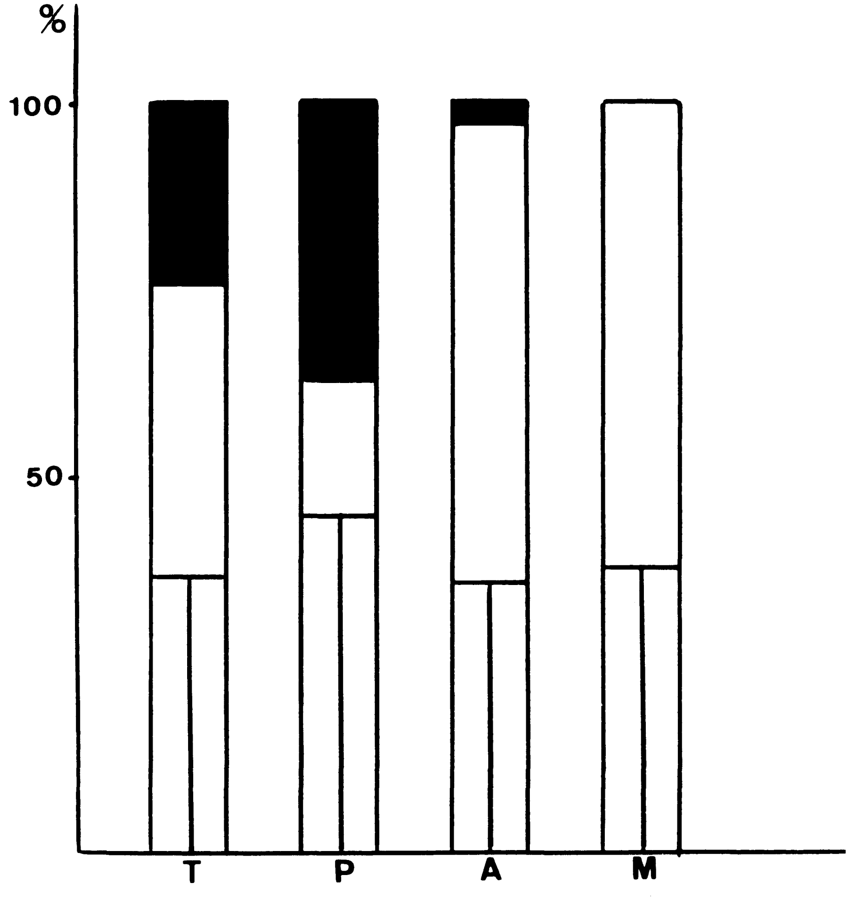

Figure 1 — Distribution of the chemical groups of diterpenes in considered regions (T = total for the genus **Dictyota**; **P** = Indo-Pacific region; **A** = Atlantic Ocean; **M** = Mediterranean Sea; = group **I**; = group **II** and = group **III**).

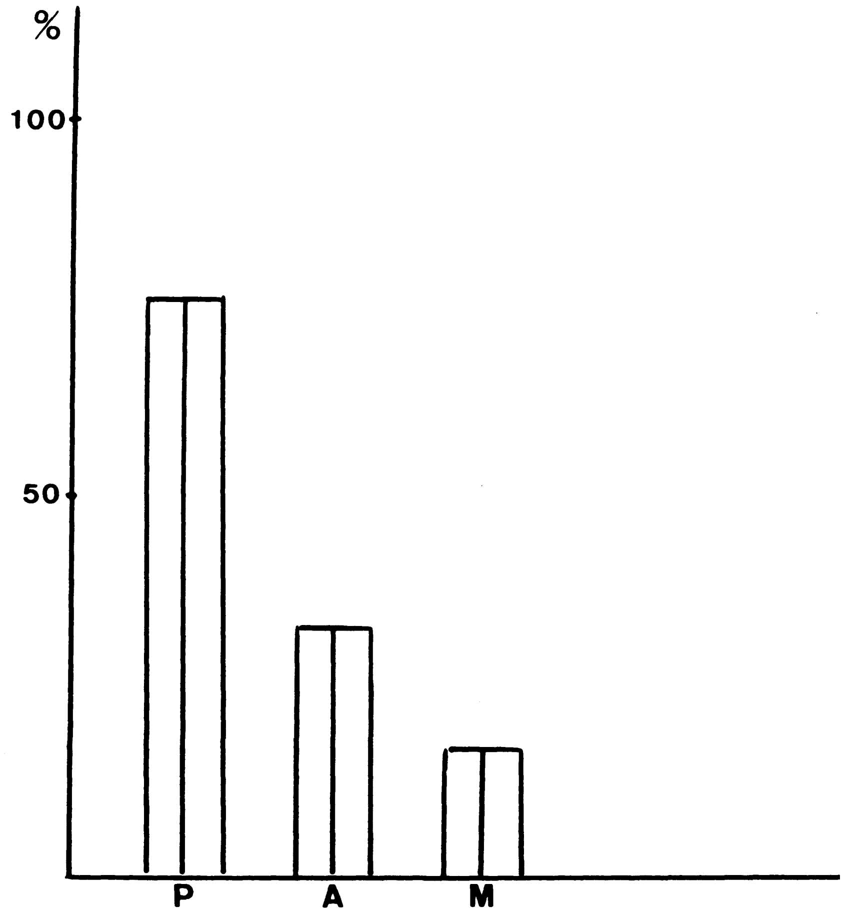

Figure 2 – Total (in%) of the products of group **I** isolated from algae of considered regions (**P** = Indo-Pacific region; **A** = Atlantic Ocean and **M** = Mediterranean Sea). 100% = total of compounds of group **I** isolated from all **Dictyota** species.

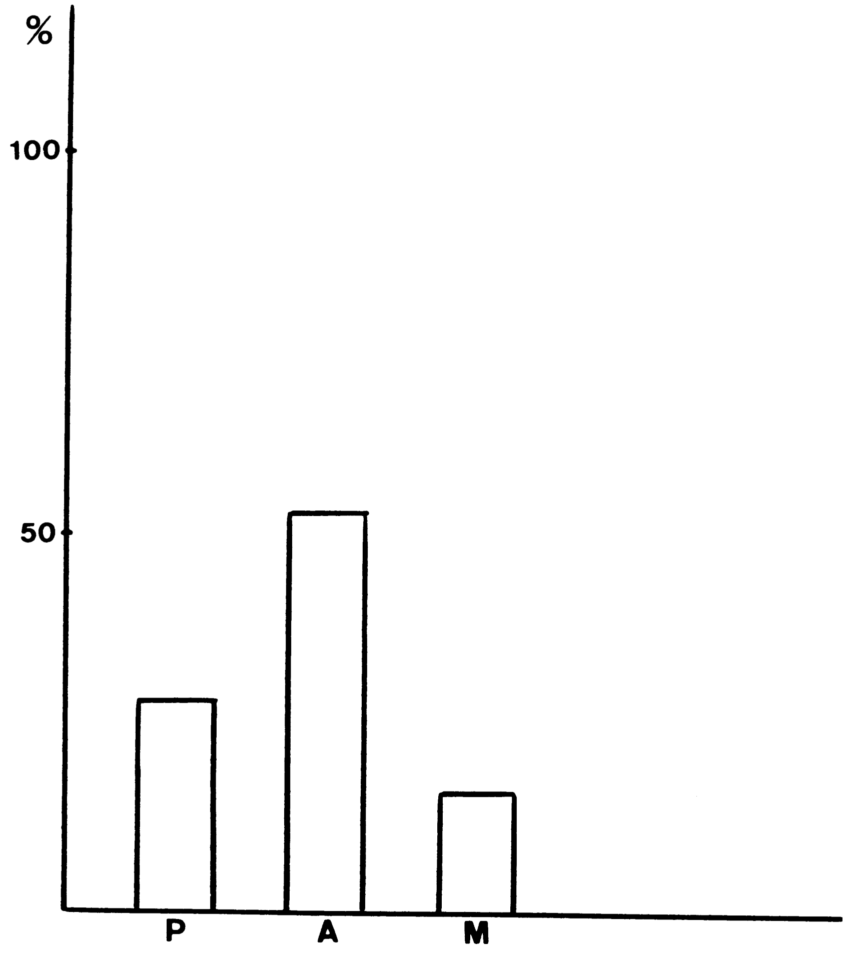

Figure 3 — Total (in%) of the products of group II isolated from algae of considered regions (P = Indo-Pacific region; A = Atlantic Ocean and M = Mediterranean Sea). 100% = total of compounds of group II isolated form all **Dictyota** species.

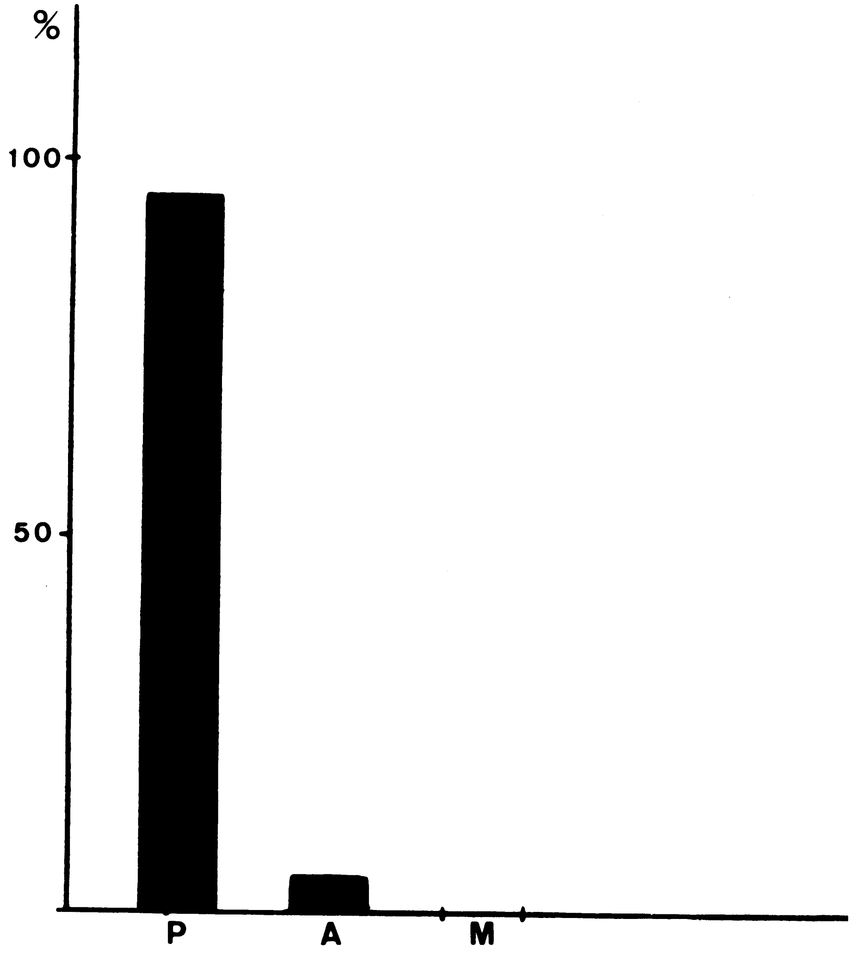

Figure 4 — Total (in%) of the products of group III isolated from algae of considered regions (P = Indo-Pacific region; A = Atlantic Ocean and M = Mediterranean Sea). 100% = total of compounds of group III isolated from all **Dictyota** species.

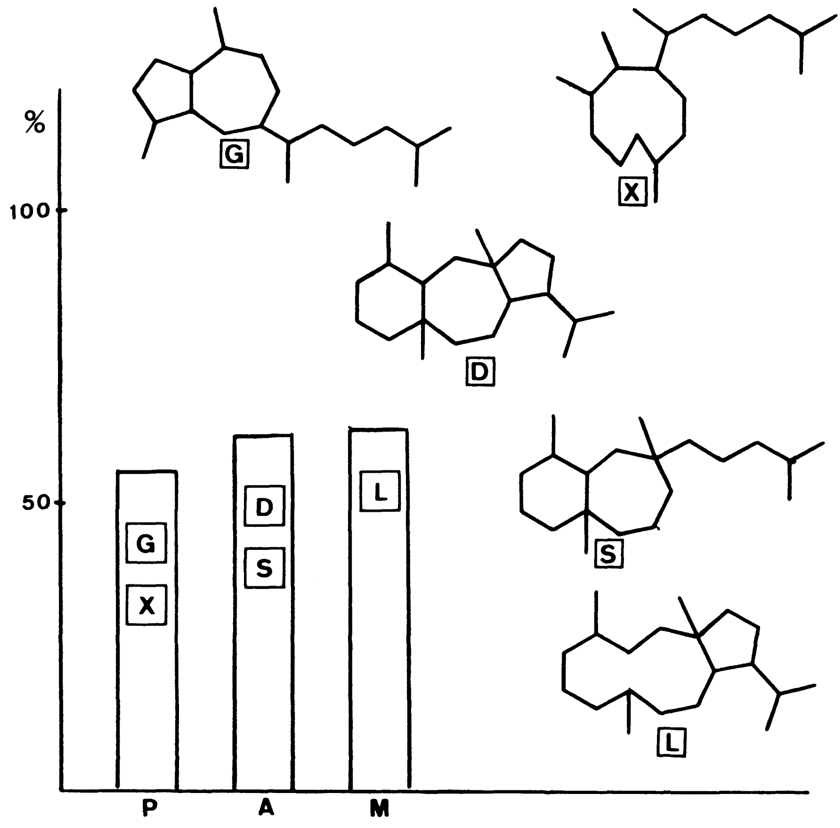

Figure 5 — Percentages of the most characteristic diterpene skeletons for each region (P = Indo-Pacific region; A = Atlantic Ocean; M = Mediterranean Sea; = xenianes; = prenylated guaianes; = dolastanes and secodolastanes and = dolabellanes).

nine species studied for the Atlantic (Table 1), 28 diterpenes (34%) were obtained belonging to 6 (35%) skeletal classes. Two varieties of a single species were studied from the Mediterranean Sea. This yielded 13 diterpenes (16%) of two (12%) different skeletons. The Indo-Pacific region is thus the one presenting the greatest strutural variety.

Table 1 — List of studied species of **Dictyota** organized following geographic regions with mention of the collection area.

Geographic Region **Studied Species** **Collection Areas (References)**
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Geographic Region	**Studied Species**	**Collection Areas (References)**
North Atlantic Ocean	**Dictyota dentata**	Boomers Beach, Barbados ALVARADO & GERWIK (1985)
	Dictyota dichotoma	Overton, S. Wales, U.K. FAULKNER et al. (1977).
	Dictyota divaricata	Roatan Island, Hog Island and Guanaja, Honduras CREWS et al. (1982)
	Dictyota divaricata	Tague Bay and St Croix, Virgin Islands SUN et al. (1981)
	Dictyota linearis	Roatan Island, Hog Island and Guanaja, Honduras CREWS et al. (1982)
	Dictyota sp	Tenerife Island, Canary Islands GONZÁLEZ et al. (1982)
	Dictyota sp	La Graciosa, Canary Islands GONZÁLEZ et al. (1983)
	Dictyota sp	Güimar, Tenerife Island, Canary Islands GONZÁLEZ et al. (1984)
	Dictyota sp	Ile de Callot, Brittany, France DEMATTÈ et al. (1985)
South Atlantic Ocean	**Dictyota cervicornis**	Angra dos Reis, Rio de Janeiro, Brazil TEIXEIRA et al. (1986 a,b)

Mediterranean Sea	**Dictyota dichotoma**	Acicastello, near Catania, Sicily, Italy AMICO et al. (1980, 1981)
	D. dichotoma var implexa	Sicily, Italy FATTORUSSO et al. (1976)
	Dictyota dichotoma	Sicily, Italy DANISE et al. (1977)
Indian Ocean	**Dictyota dichotoma**	Krusadai Island, Gulf of Mannar, India PULLAIAH et al. (1985)
North Pacific Ocean	**Dictyota acutiloba**	Kahala ana Ala Moana Reefs, Oahu, Hawaii SUN et al. (1977)
	Dictyota binghamiae	Dixon Island and Execution Rock, Barkley Sound, British Columbia, Canada PATHIRANA & ANDERSEN (1984)
	Dictyota crenulata	Kualoa Beach Park, Oahu, Hawaii KIRKUP & MOORE (1983 a,b)
	Dictyota crenulata	Cabo San Lucas, Mexico FINER et al. (1979), SUN et al. (1983)
	Dictyota dichotoma	Oshoro Bay, Hokkaido, Japan ENOKI et al. (1982 a,b, 1983 a,b,c, 1984, 1985).
	Dictyota flabellata	Sandy Beach, Puerto Peñasco, Sonora, Mexico FINER et al. (1979), ROBERTSON & FENICAL (1977)
	Dictyota indica	Yellow Sea, People's Republic of China NIANG & HUNG (1984)
	Dictyota linearis	Bay of Tosa, Japan OCHI et al. (1980 a,b, 1981, 1986)
	Dictyota masonii	Isla Guadalupe, Mexico SUN & FENICAL (1979b)
	Dictyota spinulosa	Kin, Okinawa, Japan TANAKA & HIGA (1984)
South Pacific Ocean	**Dictyota dichotoma**	Sydney area, Australia BLOUNT et al. (1982)

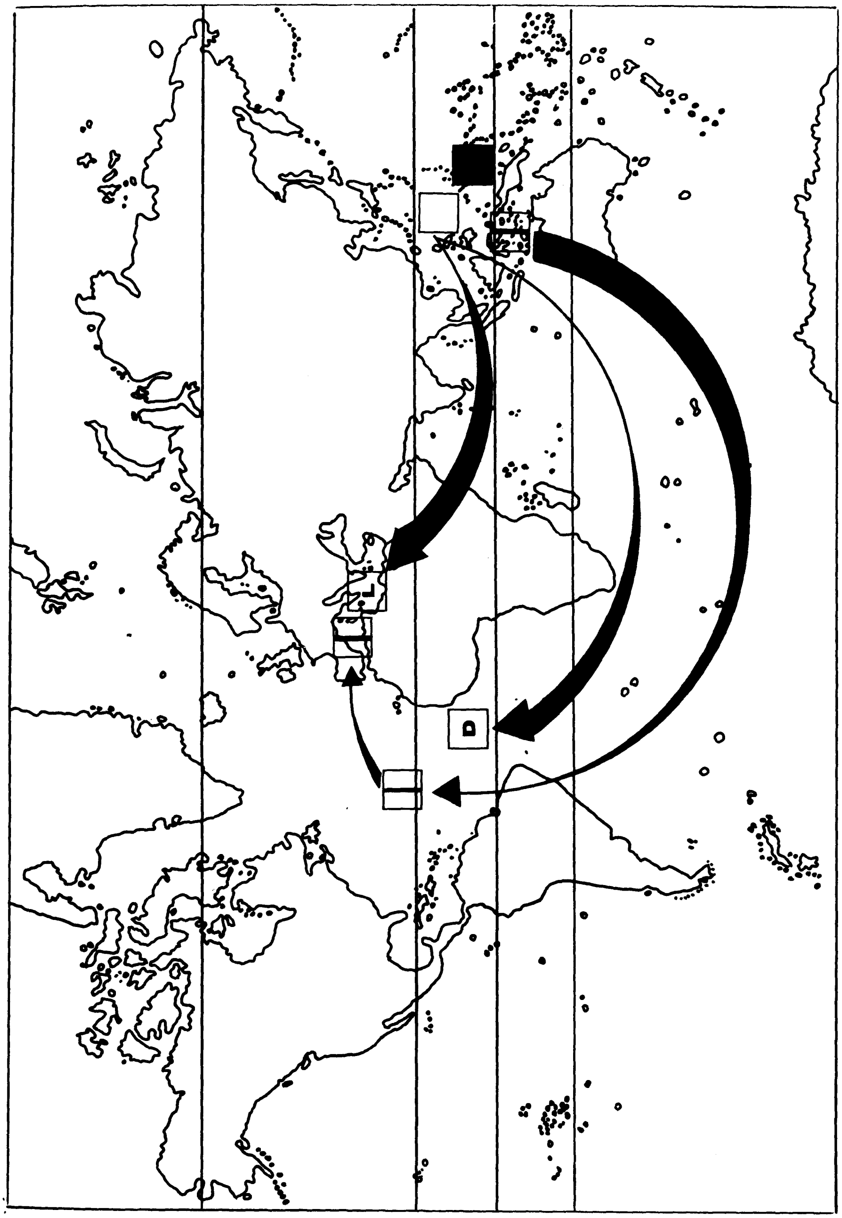
DISCUSSIONS AND CONCLUSIONS

This study on **Dictyota** diterpenes originates puzzling questions. Some of our proposals are illustrated in Map 1.

As already mentionned, the genus **Dictyota** was originated in the Indo-Pacific region, CHAPMAN & CHAPMAN (1981), where **Dictyota** species furnished 95% of the diterpenes of group III (Figure 4) and the six skeletons known for this metabolic way. On the contrary, the species from the Atlantic Ocean yielded only one xeniane of questionable structure, GONZÂLEZ et al. (1982), and diterpenes from group III did not occur at all in the Mediterranean Sea. It results to be a very reasonable hypothesis to propose that the metabolic pathway leading to diterpenes of group III should be originated in the Indo-Pacific region and should also be the most archaic. Consequently, the algae species that produce diterpenes **via** that way might well be the most primitives.

On the other hand, the invertion of the relative dominance of group III diterpenes in favour of diterpenes from group II on going from the Indo-Pacific region to the Atlantic Ocean and Mediterranean Sea is a remarkable feature. Is this phenomenon part of an evolutive strategy the impact of herbirory in the latter regions? And if so, should the diterpenes of group III be inefficient to control herbibores in the Atlantic and Mediterranean regions?

Another intriguing question is: why do dolabellane producing **Dictyota** species not also produce dolastanes that seem biogenetically related, CREWS et al. (1982), TEIXEIRA (1985), TEIXEIRA et al. (1985), TEIXEIRA & KELECOM (1987) and **vice-versa**? Interestingly, this observation may be generalized to other genera of Dictyotales that are known to produce dolabellane diterpenes: in the Pacific Ocean, **Glossophora galapagensis**, SUN & FENICAL (1979a) and **Pachydictyon coriaceum** ISHITSUKA et al. (1982); and in the Adriatic DE ROSA et al. (1984) and Mediterranean Seas, TRINGALI et al. (1984a, b, c, 1985, 1986), **Dilophus fasciola.** Nome of these genera produce dolastane or secodolastane diterpenes. In this respect, it should be remembered that the Mediterranean Sea is presently totally dependant from the Atlantic Ocean, but it is not impossible that the Mediterranean Sea still harbours plants and animals proceeding directly from the Pacific Ocean through the antique Tethys Sea, MARGALEF (1974). Are dolabellanes then the result of a metabolic pathway



Mapa 1 – Dispersion center of the genus **Dictyota** and the probable distributions of the chemical groups **I, II** and **III.**

originated in the Pacific Ocean? Such an hypothesis may explain the presence of dolabellanes in the Indo-Pacific, the absence in the Atlantic and their dominating character in the Mediterranean.

But how to explain that the Atlantic and Pacific dolastane producing species do not furnish any dolabellane, their likely biogenetic precursors? Should these skeletons be in fact originated from separate metabolic pathways? Published data on the ring junctions stereochemistry of the dolabellane and dolastane skeletons are still conflictant, TEIXEIRA (1985), TEIXEIRA et al. (1985), and do not allow to solve presently this question.

Finally, the metabolic way leading to diterpenes of group I shows universal distribution, although higher structural diversity can be observed in the Pacific Ocean. This observation allows us to suggest that this pathway is also originated in the Indo-Pacific region.

From all this, it results that the geographic distribution of **Dictyota** diterpenes parallels the biogeography of the taxon, since the highest skeletal variety was observed for the Indo-Pacific region that has been proposed, by marine botanists, CHAPMAN & CHAPMAN (1981), as the dispersion center of the genus. In addition, our data corroborate the Therory of Micromolecular Evolution of GOTTLIEB (1982), that states that colonization of new areas results in modifications of the relative importance between the various characteristic metabolic pathways of a given taxon.

ACKNOWLEDGEMENTS

V.L.T. thanks the Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) for a fellowship.

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