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CHEMOTAXONOMY OF DICTYOTALES (PHAEOPHYTA).3. THE "*Dictyopteris*" and "*Taonia*" GROUPS*.

QUIMIOTAXONOMIA DAS DICTYOTALES (PHAEOPHYTA).3. OS GRUPOS "*Dictyopteris*" E "*Taonia*".

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RESUMO

As algas pardas dos grupos "Dictyopteris" e "Taonia" fornecem em torno de 30 terpenos isolados dos gêneros *Dictyopteris*, *Stypopodium* e *Taonia*. Os sesquiterpenos e diterpenos foram separados em duas classes químicas, em função das suas origens biogenéticas, mista ou não. Foram calculados índices de similaridade segundo Soerensen e os metabólitos foram caracterizados pelos índices de oxidação e de esqueleto. As médias dos índices, calculadas para cada táxon, mostraram que os terpenos são bons marcadores taxonômicos e que seria mais tendencioso que se separasse a ordem Dictyotales em três famílias.

PALAVRA CHAVE: Quimiotaxonomia, algas pardas, Dictyotales, *Dictyopteris*, *Stypopodium*, *Taonia*, sesquiterpenos, diterpenos, terpenos mistos.

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ABSTRACT

Brown algae of the "*Dictyopteris*" and "*Taonia*" groups have yielded about 30 terpenes that have been isolated from species of the genera *Dictyopteris*, *Stypopodium* and *Taonia*. Sesquiterpenes and diterpenes have been separated each into two chemical classes dipending on their biogenetic origin, mixed or not. Similarity coefficients following Sorensen have been calculated, and metabolites have been characterized by oxidation and skeleton indices. The mean values of these indices, calculated for each taxon, indicated that terpenes are suitable taxonomic markers and that the order Dictyotales should be divided into three families.

KEY-WORDS: Chemotaxonomy, brown algae, Dictyotales, *Dictyopteris*, *Stypopodium*, *Taonia*, sesquiterpenes, diterpenes, mixed terpenes.

INTRODUCTION

Dictyotales are brown algae of the division Phaeophyta that are mainly distributed in tropical and sub-tropical waters. The order Dictyotales includes 16 genera that all belong to a single family, Dictyotaceae (PAPENFUSS 1977). Phytochemical investigations showed deep differences between its representatives, and indicated, at least, three chemical groups referred to as the "*Dictyota*", "*Dictyopteris*" and "*Taonia*" groups (FENICAL 1980). In previous studies, we showed that diterpenes are valuable taxonomic markers of the genus *Dictyota* and also of the "*Dictyota*" group (TEIXEIRA & KELECOM 1988, 1989). In this work, we report on the chemotaxonomic analysis of terpenes from the "*Dictyopteris*" and "*Taonia*" groups. The usefulness of these metabolites as taxonomic and phyllogenetic markers is discussed.

METHODS

Literature data on terpenoids from pertinent algae has been examined until November 1988. A biogenetic map was then built up, following commonly accepted biosynthetic steps for sesquiterpenes (Fig.1), and following the proposal of GONZALES and co-workers (1982a) for diterpenes (Fig.2). Since no biosynthetic work has been published this proposal, although reasonable, has to be considered as theoretical speculation.

The semi-empiric statistical methodology developped by GOTTLIEB and co-workers (GOTTLIEB 1982) was used for chemotaxonomic purposes. Terpenes were characterized as previously described (TEIXEIRA & KELECOM 1988) by two indices: the skeleton index (SI) relative to skeleton complexity, and the oxidation index (OI) relative to the functionalization. For SI calculations, farnesol and geranylgeraniol-6-toluhydro-quinone were chose as common precursors for sesquiterpenes and mixed diterpenes respectively. Each taxon was then represented by the indices of evolutive advancement for skeleton (IAs) and oxidation (IAo) that were obtained as the arithmetic means of SI and OI values observed for all the terpenes found in considered taxon (GOTTLIEB 1982).

The affinities between species were deduced from the similarity coefficients (S) calculated following Sorensen (1948), using terpene skeletons as character (TEIXEIRA 1985). This index was preferred over others, since present common characters are considered more significant than the absent characters.

Finally, the areas of algae collection were taken into consideration for tentative biogeographic and phyllogenetic analyses.

RESULTS

Chemical data were available for seven species of the genus *Dictyopteris*, one of the genus *Stypopodium* and two of the genus *Taonia*.

The "*Dictyopteris*" chemical group includes only representatives of the *Dictyopteris* genus. A number of investigations have been concerned only with odoriferous hydrocarbons (MOORE 1977 MOORE & YOST 1973, MOORE et al. 1968, 1974, PETTUS & MOORE 1970, 1971, YAMADA et al. 1979, 1986), some of which act as sexual pheromones (BOLAND & MUELLER 1987, KAJIWARA 1981, KAJIWARA et al. 1980, 1982, MOORE 1976, YAMADA et al. 1980), and will be the object of a separate work (PITOMBO et al. 1989). Other studies described sulfur containing metabolites such as polysulfides, thiols and thioesters (MOORE 1971, MOORE et al. 1972, ROLLER & MOORE 1971), and sesquiterpenes (e.g. KUROZAWA et al. 1966) for the which the biological function has not been firmly established. Sterols that are constituents of cell membranes (GOAD 1978), and polyhydroxyphenols (tannins) that are largely distributed in the divison Phaeophyta (RAGAN & GLOMBITZA 1986) have also been reported. The latter are related to herbivory control and will be commented separately (PE-

REIRA et al. 1989).

Only terpenes will be considered in this study. They are been isolated from two of the seven species of *Dictyopteris* studied chemically: *Dictyopteris zonarioides* (=*D. undulata*) and *D. divaricata*. Terpenes of the former species are from mixed biosynthetic origin, and are closely related to the sponge metabolites of the chromazonarol series (MINALE 1978). Their role as antifeedant has been suggested (FENICAL 1980). Up to now, 25 sesquiterpenes have been isolated from *D. divaricata* and *D. zonarioides*. They belong to two main classes depending on wether they are (class II) or not (class I) of mixed biosynthetic origin. Sesquiterpenes from class I all derive from a 1,10 cyclization of t,t-farnesol leading to a germacrane-type intermediate the which furnishes, by a known sequence of transcyclization steps, or via a Cope rearrangement, the cadinane, copaane, cubebane, selinane and elemane skeletons (Fig.1). Fifteen substances of this class have been described, all produced by *D. divaricata* (FENICAL et al. 1972, IRIE et al. 1964, KUROSAWA et al. 1966, SUZUKI et al. 1981). Sesquiterpenes from class II result from coupling of a farnesane-type precursor to an acetate derived para-hydroquinone or para-hydroxybenzoic acid moiety, with or a without further cyclization to yield substituted drimane or farnesane sesquiterpenes. Ten such compounds have been found, all of them in *D. zonarioides* (CIMINO et al. 1975, DAVE et al. 1984, FENICAL & SIMS 1973, FENICAL & McCONNELL 1975, OCHI et al. 1979a, 1979b).

The "*Taonia*" group includes representatives of the genera *Taonia* and *Stypopodium* that produce diterpenes of mixed biosynthetic origin (class II) or not (class I). The latter class is known for a single furane-containing diterpene isolated from *Taonia australasica* (MURPHY et al. 1981). Sixteen metabolites have been reporteds in class II. They all derive from a geranyl-geraniol-6-toluhydroquinone precursor as shown in Fig.2. Two simple tetraprenyl-toluhydroquinones have been reported from *S. zonale* (GERWICK et al. 1981, 1985) and have been found to be closely related to metabolites from *Sargassum* species (Fucales, Phaeophyta). Cyclization of the precursor yield the unknown tetracyclic intermediate ("A"). Subsequent methyl rearrangements and A-ring oxidative cleavage of "A" furnishes metabolites of the uncommon atomaric acid series, observed in *T. atomaria* (GONZALES et al. 1974, 1982) and *S. zonale* (GERWICK et al. 1985). On the other hand, ether formation from "A" may yield the pyrane-type terpenes of the taondiol series (GONZALEZ et al. 1971, 1972, 1973) or the hydrofurane-type terpenes of the stypodiol series

(GERWICK et al. 1979), the former distributed in *Taonia* (GONZALEZ et al. 1982b, 1984) and *Stypopodium*, the latter restricted to *S. zonale* (GERWICK et al. 1979).

Table 1 shows the terpene distribution (i.e. number of metabolites and skeleton types) in the "*Taonia*" and "*Dictyopteris*" groups, together with the areas of algae collections.

The similarity matrix following Sorensen is shown in Table 2. Obviously, the S value was zero between any pair of species of the "*Dictyopteris*" and "*Taonia*" groups since these groups do not produce the same terpene skeletons. The paucity of chemical information on *T. australasica* also leeded to a zero similarity value when compared with species within the "*Taonia*" group. A low similarity index (S = 0.22) was observed between both species of the *Dictyopteris* genus, due to the co-occurrence of a cardinane-type sesquiterpene. A significant similarity value (S = 0.80) was observed between *S. zonale* and *T. atomaria* and resulted from the co-occurrence of taondiol- and atomaric acid-like substances. This observation was also evident from graphic comparison of the taxonomic indices (Fig. 3) calculated for *T. atomaria* (IAs = 0.21, IAo = -1.17) and *S. zonale* (IAs = 0.14, IAo = -1.23). However, *Taonia* metabolites were at the same time more oxidized and more complex than those from *Stypopodium*. Since these indices are mean values, they were not significant for *T. australasica* (IAs = 0.05, IAo = -1.30) for the which only one compound had been reported (MURPHY et al. 1981).

Only very few informations were available for biogeographic considerations. The genus *Dictyopteris* includes about 13 species that are largely distributed in warm waters in several parts of the world. On the contrary, the *Taonia* genus, with about 3 species, and the *Stypopodium* genus, with about 5 species, both present more retricted geographic distribution. Thus, all metabolites described for *Dictyopteris* were obtained from species collected in the Pacific Ocean; metabolites from *Taonia* were isolated from an Atlantic species, with the exception of the peculiar furano-diterpene from *T. australasica* obtained from a Pacific species. *S. zonale* was the only species that yielded terpenes from populations of the Pacific and Atlantic Oceans. Interrestingly, geranylgeraniol-6-toluhydro-quinone, the common precursor to all diterpenes of mixed biosynthetic origin in the "*Taonia*" group, has been found only in populations of *S. zonale* (GERWICK et al. 1985), but from both the Pacific and Atlantic Oceans.

DISCUSSION

Although the number of available chemical information on terpenes from algae considered in this work is small when compared to the "Dictyota" group (TEIXEIRA & KELECOM 1989), it may be stated that terpenes are suitable taxanomic markers for the order Dictyotales.

Thus at least three chemical groups can be observed. The "Dictyota" group, with six chemically studied genera (*Dictyota*, *Dilophus*, *Glossophora*, *Pachydictyon*, *Spatoglossum* and *Stoechospermum*) is characterized by an array of simple diterpenes, mainly with polycyclic skeletons that are exclusive from marine organism. None of these terpenes are from mixed biosynthetic origin (TEIXEIRA & KELECOM 1989).

On the contrary, algae from the "*Taonia*" group (genera *Stypopodium* and *Taonia*) produced diterpenes from mixed biosynthetic origin. The acetate part of these metabolites is present as a toluhydroquinone moiety. A toluquinone may be observed; but stypoldione has been shown to be an isolation artifact (GERWICK et al. 1985) and has not been therefore considered in this study, although this compound is of particular pharmacological interrest (O'BRIEN et al. 1984). The chemical affinity observed between both genera of this groups was in agreement with morphological data that indicates that *Taonia* and *Stypopodium* are indeed related (PAPENFUSS 1977). One species of the group, *T. australasica*, did not obey the general rule pointed above, and this may be related, if not to a wrong identification of the alga, at least to the very peculiar Australian marine flora that includes many endemic species (ALLENDER & KRAFT 1983) and that also produce "endemic metabolites". This has already been observed with *Dictyota dichotoma* from the Sydney waters that yielded cycloxeniane and dichotomane diterpenes, two skeletons restricted to that population of *D. dichotoma* (TEIXEIRA et al. 1989).

Finally, the "*Dictyopteris*" group produced sesquiterpenes and not diterpenes. These may, in addition, be or not from mixed biogenetic origin. When so, the acetate moiety is present as an hydroquinone or as a para-hydroxybenzoic acid. Drimane-related sesquiterpenes have been observed that are closely related to some sponge metabolites (MINALE 1978). Of course, no direst biological interactions may be invoqued, being this probably just an example of parallel evolution beyond the selective pressure. Similarly, the polyprenylhydroquinones from *Dictyopteris zonarioides* are realted to metabolites from the more evoluted *Sargassum* genus. Should this again be parallel evolution or is it indicative of the evoluted character of the genus *Dictyopteres* already evidenced by its median rib? Another phyllogenetic suggestion derived from Fig. 3. Indeed, it is generally accepted that more evoluted components are to be observed on the diagonal, far from the origin (GOTTLIEB 1982). Hence, one may suggest that *Taonia atomaria* might well be more evoluted than *Stypopodium zonale*. All this has to be considered as extremely hypothetic, but since *T. atomaria* is more typically an inhabitant from the Atlantic Ocean, known to be younger than the Pacific one, this proposal makers sense.

From all this, one may suggest that the order Dictyotales, with only one family Dictyotaceae (PAPENFUSS 1977), should be split into three families, according to the terpene composition. However, one need to remember that a good deal of genera from this order still lacks chemical information, either totally or in part. Some new views may thus arise in the future. For example, from the available literature data, it is not impossible that a fourth group will appear: the "*Zonaria*" group that should include the genera *Zonaria* and *Lobophora*, both source of phenolic acetogenins (AMICO et al. 1982, GERWICK & FENICAL 1982, TRINGALI & PIATTELLI 1982), that are surprisingly closely related to metabolites from *Cystophora* spp (Fucales, Phaeophyta) (e.g. RAVI et al. 1982). Further studies are necessary to obtain a complete chemotaxonomic representation of the Dictyotales, and also to discuss on biogeographic informations related to the groups considered in this work, in the same way as it has been done for the genus *Dictyota* (TEIXEIRA & KELECOM 1987).

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TABLE 1 - Terpene distribution, skeletons and algae distribution.

SESQUITERPENES FROM THE "*DICTYOPTERIS*" GROUP

Species \ Skeletons	Area	Ocean	Class - I					Class-II		References
			CAD	COP	CUB	ELE	SEL	Acyclic	Cyclic	
Dictyopteris divaricata	Japan	Pacific	6	1	3	1	3	-	-	23,27,50
Dictyopteris zonaroides	Japan	Pacific	-	-	-	-	-	2	8	4,5,8,9,39,40
	México	Pacific	1	-	-	-	-	-	1	8
	California	Pacific	-	-	-	-	-	-	1	8

DITERPENES FROM THE "*TAONIA*" GROUP

Species \ Skeletons	Area	Ocean	Class - I	Class-II		References
				Acyclic	Cyclic	
Stypopodium zonale	Caribbean	Atlantic	-	2	7	10,11,13
	Micronesy	Pacific	-	2	3	11,13
Taonia atomaria	Canary I.	Atlantic	-	-	9	15,17,a 19,21
Taonia australasica	Australia	Pacific	1	-	-	37

CAD= cardinane, COP= copaane, CUB= cubebane, ELE= elemane, SEL= selinane

TAXA	A	B	C	D	E
A: *Dictyopteris divaricata*	1,00				
B: *Dictyopteris zonaroides*	0,22	1,00			
C: *Stypopodium zonale*	zero	zero	1,00		
D: *Taonia atomaria*	zero	zero	0,80	1,00	
E: *Taonia australasica*	zero	zero	zero	zero	1,00

TABLE 2 - Similarity matrix (Sørensen, 1948) of species from the "Taonia" and "Dictyopteris" groups.

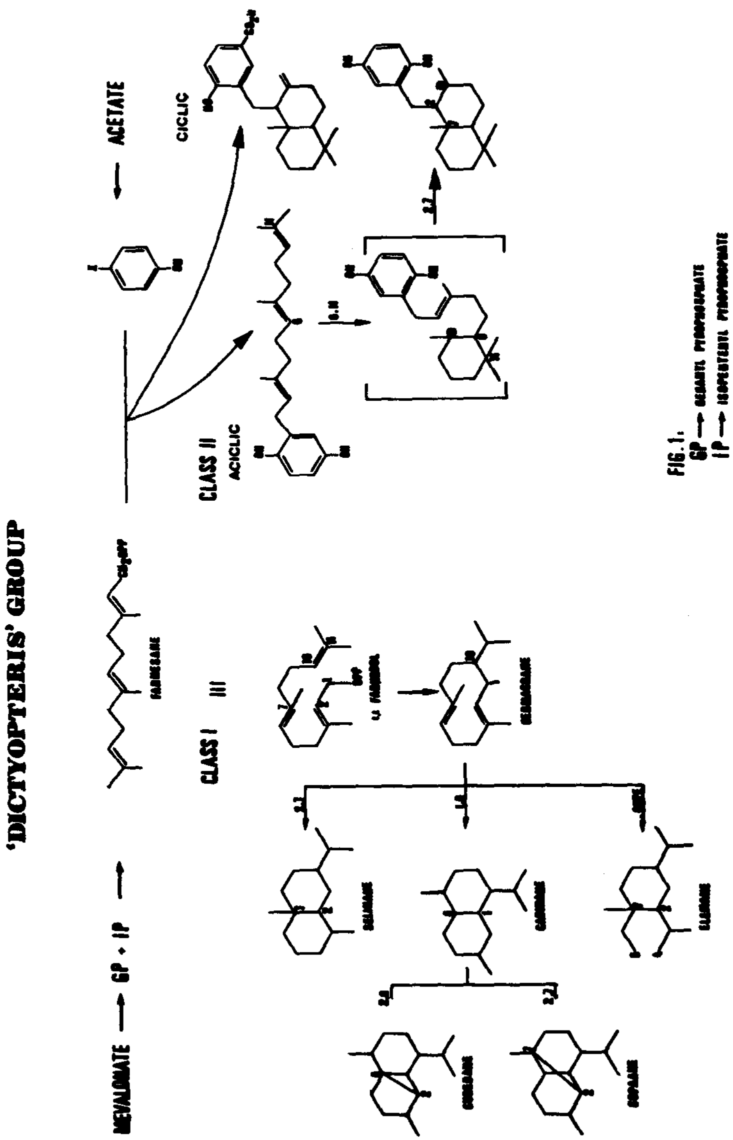

FIG. 1 - Biogenetic map of sesquiterpenes from the "Dictyopteris" group

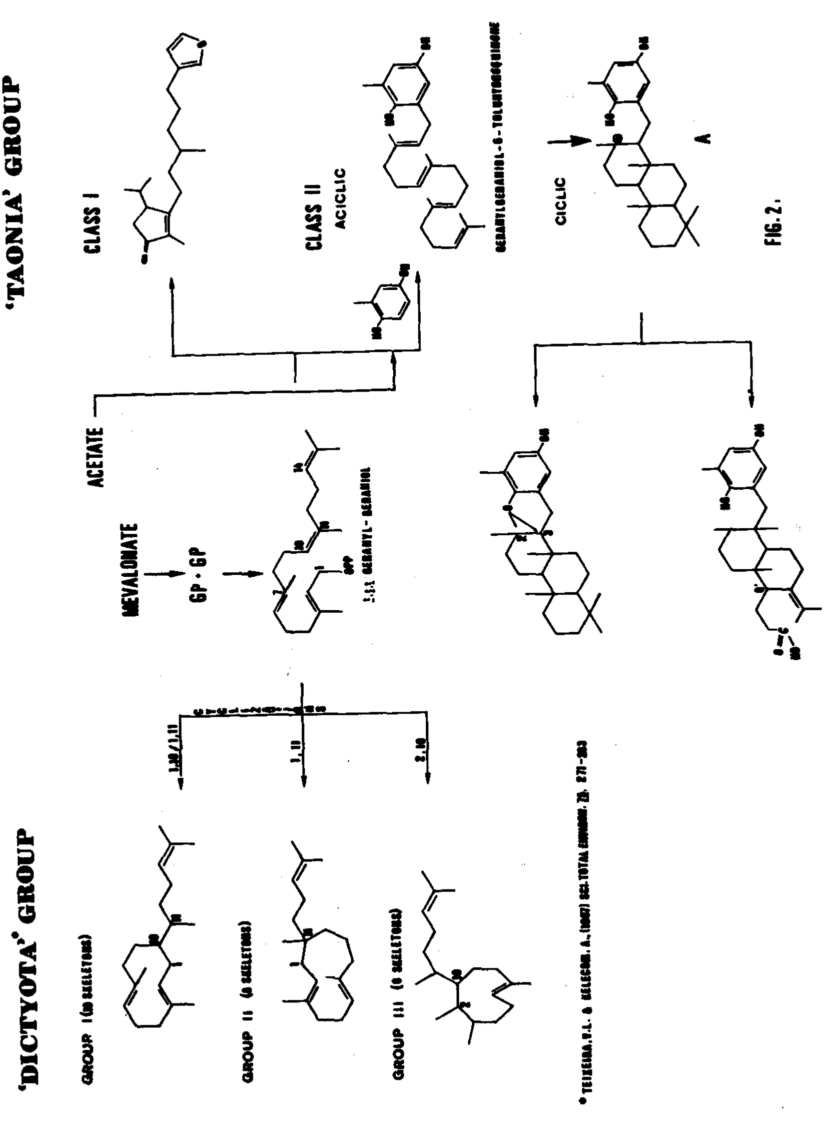

FIG. 2 - Biogenetic map of sesquiterpenes from the "Dictyota" and "Taonia" groups

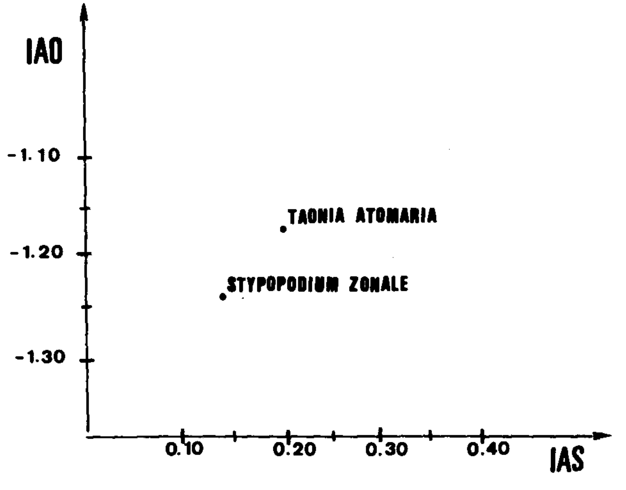

FIG. 3 - "Taonia" group: IAS versus IAO