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CHEMICAL INDEXES CALCULATED FOR 8,11,13-TRIENABIETANE DITERPENOIDS ISOLATED FROM SWARTZIA SPECIES
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Swartzia, *Bobgunnia*, *Bocoa*, *Candolleodendron*, *Trischidium*, *Cyathostegia*, and *Ateleia* [1,12, 13].

Cladistic analyses showed the group of *Myrospermum*, *Myroxylon* and *Myrocarpus* of Sophoreae to be associated with the Aldinoid clade of the Swartzieae and closely to Swartzieae *sens. strict*. [12]. The reclassification of Swartzieae *sens. strict.*, and realignment of the remaining swartzioid genera in other tribes, needs to be corroborated by further evidence [1, 13].

On the other hand, evolutionary changes in plants can also be evaluated through the chemical structures of the special metabolites found in them, based on the disparity (related to the biogenetic route) and the diversity of their molecular structures [14]. The methodology is very attractive because it does not imply knowledge of the complete biogenetic route of metabolites and has already indicated evolutionary tendencies for the *Swartzia* species that produce isoflavonoids [15]. In this paper, the methodology is used to suggest evolutionary directions for two *Swartzia* species that, instead of isoflavonoids [16-20], furnish terpenoids.

Methodology

Disparity Evaluation- The disparity of metabolites reported in *Swartzia* genera were evaluated by comparing their chemical structures since, according to Gottlieb's methodology [14], disparity in the molecular structure of special metabolites indicates an evolutionary move and occurs by the replacement of compounds generated from the shikimic acid/acetate biogenetic route by compounds generated from the acetated route (or mevalonic acid route).

Accordingly, the species were separated into two groups, those that furnished special metabolites originating from the shikimic acid/acetate route - the isoflavonoids, and those that furnished compounds formed by the mevalonic acid route - the terpenoids (Table 1).

Table 1. Correlation between chemical data reported for *Swartzia* studied phytochemically and botanic classification (Cowan 1967), phylogeny reported in the current literature (Torke & Schaal 2008).

	Cowan 1967		Torke & Schaal 2008	Araujo 2007; Braz Filho et al. 1980; Osawa et al. 1992; Dubois et al. 1995, 1996	Magalhães et al. 2005; Orphelin et al. 1996	Borel et al. 1987; Abdel-Kader et al. 2000; Magalhães et al. 2003
Species	Section	Series	Clade	Isoflavonoids	Diterpenoids	Saponins
S. ulei	Swartzia	Benthamianae		+		
S. laevicarpa	Swartzia	Benthamianae	benthamioid	+		
S. leiocalycina	Swartzia	Recurvae	recurvoid	+		
S. polyphylla	Swartzia	Orthostyleae	orthostyloid	+		
S. schomburgkii	Swartzia	Orthostyleae	orthostyloid			+
S. apetala	Swartzia	Tounateae	tournateoid	+		+
S. langsdorffii	Swartzia	Recurvae	acutifolioid		+	+
S. arborescens	Possira	Possira	possiroid		+	
S. simplex	Possira	Possira / Unifoliolatae	possiroid			+

The initial part of proposed route is very similar to that reported for the C-12 methoxy derivative of ferruginol [23] including a 1,2-methyl *si* migration. However, the shift now proposed occurs between C-13 and C-14, and not between C-13 and C-15, and is reinforced by the detection of C-14 methylated 8,11,13-trien-abietane compounds in the species *Myrocarpus frondosus* [24], a species of the Sophoreae tribe, which is closely related to *Swartzieae sens. strict.*.

Some cyclization processes are proposed leading to the compounds that were isolated from *Swartzia* species and from the species *Myrocarpus frondosus*. The metabolites carbon skeletal difference is in ring D, as, in case of the metabolites furnished by *M. frondosus* , ring D would be formed by an oxidative cyclization reaction between C-16 and C-12, allowed by the absence of the protective C-12 methoxy group of swartziarboreols. In the case of swartziarboreols, however, oxidative steps would occur before a final cyclization reaction between C-16 and C-17 that would give rise to the isocoumarin ring D. Then, the other compounds would be generated by a series of oxidative and methylation processes.

However, when Gottlieb's chemical index methodology is applied, a knowledge of such biogenetic pathways of special metabolites is not necessary since the evolutionary evaluation is made by means of two chemical indexes, the oxidative evolutive advance index, EA_O, and the skeleton complexity evolutive advance index, EA_E, of each plant species.

The indexes EA_O and EA_E are found by calculating the averages: $EA_O = (\Sigma\ O) / N$ and $EA_E = (\Sigma\ E) / N$, where the value N refers to the number of metabolite occurrences, and the O and E values are the chemical indexes that quantify the oxidative degree of the molecular structures (O) and the carbon skeleton specialization (E) of each metabolite.

The oxidative degree indexes (O) were calculated by the equation, $O = (x-h)/ n$, where the letters n, h and x refer, respectively, to the total number of carbon atoms (n), the number of C-H bonds (h) and the number of C-heteroatom bonds (x) of the terpenoid skeleton, while the carbon skeleton specialization indexes (E) were calculated by comparing the carbon skeleton of each diterpenoid chemical structure in focus with the carbon skeleton of a hypothetic common precursor (compound **A**; Fig. 1), by using the equation: $E = (q + f + c + u) / n$, where the letters n, q, f, c, and u, represent, respectively, the total number of carbon atoms (n), the number of C-C bonds broken (q), the number of C-C bonds formed (f), the number of rings formed with a heteroatom, (c), and the number of additional carbon atoms (u). Table 2 shows the O and E values found for ten compounds identified from *S. langsdorffii*. The same calculations were applied to the five diterpenoids reported for *S. arborescens* [25] (Table 3). Finally, the oxidative advance index, EA_O, and the skeleton specialization advance index, EA_E, of each species are displayed in Table 4.

Table 3. Oxidative evolutive index values (O), calculated for the swartziarboreols **A-E** isolated and identified in the extracts of *S.arborescens* (Orphelin et al. 1996).

Compound	O*	E**
swartziarboreol A	-0.62	0.00
swartziarboreol B	-0.52	0.00
swartziarboreol C	-0.71	0.00
swartziarboreol D	-0.57	0.00
swartziarboreol E	-0.57	0.00

* O = x-h/ n, where the letters, refer, respectively, to the total carbon atoms (n), the C-H bonds (h) and the C-heteroatom bonds (x) of the diterpenoid skeleton. ** E = Carbon skeleton specialization chemical index.

Table 4. Values for oxidative evolutive advance and skeleton complexity evolutive advance, EA_o and EA_E, calculated using the chemical index values found for the metabolites identified in the species *S. langsdorffii* and *S. arborescens.*

Species	EA_o [a]	EA_E [b]
S. langsdorffii	-0.94	0.00
S. arborescens	-0.60	0.00

[a] $EA_o = \Sigma$ O/n [b] $EA_E = \Sigma$ E/n; n = metabolite occurrences.

Results and Discussion

Disparity Evaluation- Comparing the chemical structures of metabolites reported for *Swartzia* species (Table 1) it is possible to observe two groups characterized by the presence of isoflavonoids or terpenoids. Phytochemically studied *Swartzia* species that furnished diterpenoids and triterpenoidal saponins (*S. arborescens* [25], *S. simplex* [26], *S. schomburgkii* [27] and *S. langsdorffii* [21, 22, 28]) are more recent concerning the evolutionary aspects, since their metabolites were generated by the mevalonic acid route while the remaining species produced isoflavonoids that are formed by the shikimic acid/ acetate route.

Considering the clades obtained by **Torke & Schaal** [12], the presence of these substances could be used, in addition to other data, to define the *Swartzia* clades: possiroid and acutifolioid clades characterized by terpenoids, and orthostyloid and benthamioid clades characterized by flavonoids (Table 1). In this sense, the systematic position of *S. schomburgkii* is doubtful, appearing with 58% maximum parsimony bootstrap support in a combined chloroplast and nuclear sequences tree [12, Fig. 3]. In the trees obtained in separate searches of combined chloroplast sequence data and ITS sequences, *S. schomburgkii* and *S. polyphylla* remain in distinct clades [12, Fig. 1 and 2]. If the absence of diterpenoids in *S. simplex* would be confirmed, this would point out the applicability of subcategories in *Possira* classification.

Diversity Evaluation- The second evaluation was made by analysis of the diversity of the chemical structures of fifteen 8,11,13 *-trien-*-abietane diterpenoids identified from the species *S. arborescens* and *S. langsdorffi*.

Different from isoflavonoid chemical index calculations, the chemical indexes for terpenoids, as mentioned above, is evaluated by the oxidative degree (O) and by the carbon skeleton specialization (E) of their molecular structures. Table 2 shows the values of the chemical indexes obtained for *S. langsdorffii* metabolites. The same rationalization and kind of calculations led to the values displayed in Table 3 for the metabolites of *S. arborescens*.

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Resumo: A análise das estruturas moleculares dos compostos isolados de nove plantas do gênero *Swartzia* mostrou que, na produção de metabólitos especiais, algumas plantas abandonaram a rota do ácido shikimic/acetato e adotaram a rota do ácido mevalônico. Esta mudança é fator indicativo de que essas espécies são evolutivamente mais recentes. Já a diversidade de estruturas moleculares encontrada nos dezesseis diterpenoides 8,11,13-trien-abietanos, chamados de swartziarboreols, identificados em *S. arborescens* e *S. langsdorffii*, permitiu atribuir a cada uma dessas espécies um índice químico, mostrando que os de *S. arborescens* são mais recentes do que os de *S. langsdorffii*. Os resultados sugerem que as espécies da seção *Possira* devam ocupar uma posição derivada em *Swartzia*.

Palavras-chave: Leguminosas, Sistematica do gênero *Swartzia*, evolução de plantas, índices químicos, quimiotaxonomia.

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