

LIMONOIDS, ALKALOIDS AND CHROMONES FROM *DICTYOLOMA VANDELLIANUM*, AND THEIR CHEMOSYSTEMATIC SIGNIFICANCE

Paulo C. Vieira, Ana R. Lázaro, João B. Fernandes e M. Fátima das G.F. da Silva

Departamento de Química, Universidade Federal de São Carlos, C. Postal 676, CEP 13560 São Carlos – SP – Brazil

From dichloromethane extract of roots of *Dictyoloma vandellianum* were isolated two chromones identified as 6-(3-methylbut-2-enyl) allopteroxylin and sorbifolin. The first compound was previously isolated from the same species, and the last one, for the first time from this genus.

INTRODUCTION

Dictyoloma, a genus containing only two species, has been the subject of discussion due to the difficulty of positioning it in either Rutaceae or Simaroubaceae. Engler^{1,2} first included *Dictyoloma* in the Simaroubaceae, but later removed it to Rutaceae, classifying *Dictyoloma* as the single genus in the subfamily Dictyolomatoideae.

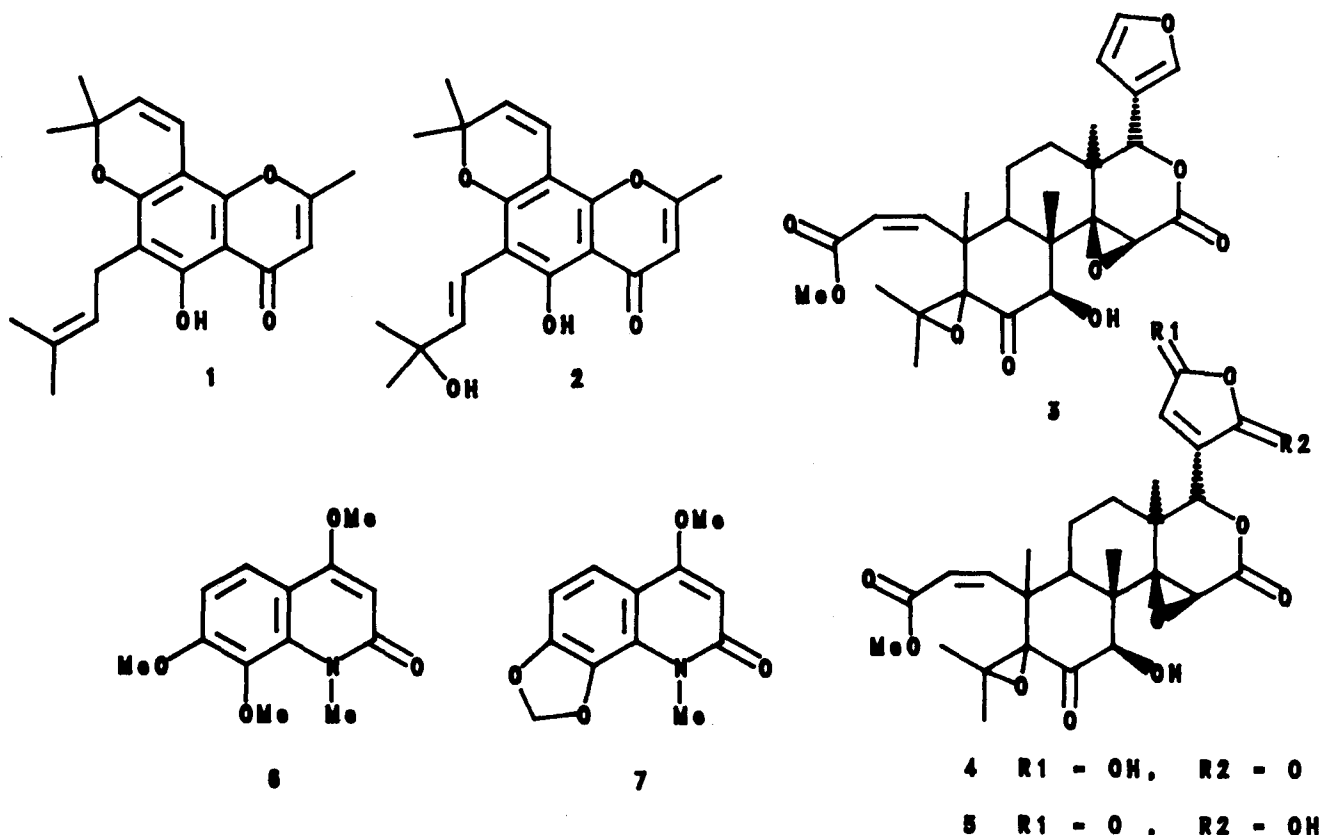
Recently³ we have described the isolation and identification of the limonoids 3, 4 and 5, besides the quinolone alkaloids 6 and 7 from *D. vandellianum*. The occurrence of these compounds was important for a better positioning of the genus in the Rutaceae family. In this paper we deal with the isolation and identification of two chromones from the roots of *D. vandellianum*. We also discuss the chemosystematic significance of the presence of limonoids, alkaloids and chromones in *Dictyoloma*, for a better understanding of its chemotaxonomic position in the Rutales.

RESULTS AND DISCUSSION

The dichloromethane extract of *D. vandellianum* has yielded two chromones. These chromones showed to have very close structures based on spectroscopic analysis. The ¹H NMR spectra showed for the two compounds signals referring to a methyl group (δ 2.30 \pm 0.06) and a 2,2-dimethylchromene ring (δ 1.48s, 6.56 \pm 0.06 *d*, 5.48 \pm 0.05 *d*). Further signals in spectrum (δ 1.69, 1.81, 3.40 and 5.20) revealed for 1 the presence of 3,3-dimethylallyl moiety attached to the C-6 in the chromone skeleton. The presence of a 3,3-dimethylallyl group attached to C-6 was confirmed through the cyclisation reaction yielding additional ring.

The only difference observed for compound 2 is the replacement of the 3,3-dimethylallyl group at C-6 in 1, by a *trans*-3-hydroxy-3-methyl-but-1-enyl in 2.

The comparison of the data above with those from the literature^{4,5} allowed us to propose the structure of 6-(3-me-



thylbut-3-enyl) allopteroxylin for 1 and sorbifolin for compound 2.

Compound 1 was isolated before from another source of *D. vandellianum*⁴ and compound 2 from *Spathelia sorbifolia*⁵.

CONCLUSION

Recently, Waterman⁶, based on the distribution of secondary metabolites proposed a phylogenetic diagram of the Rutales. From this diagram it is clear the association between Cneoraceae, Pteroxylaceae, *Harrisonia* and Spathelioideae. Cneoraceae is a small family with two genera, containing coumarins and chromones, besides limonoids. Pteroxylaceae is characterized mainly by the presence of coumarins and chromones, lacking limonoids. *Harrisonia* has recently been placed in the Simaroubaceae, however it contains chromones and limonoids, lacking the principal characteristic of Simaroubaceae, the quassinoids.

More recently⁷, the chemosystematics of Rutaceae was reviewed on the basis of updated surveys of various secondary metabolites and their biosynthetic derivation. Starting from obviously natural groups of genera (or single genus) as basic taxonomic entities a new system with informal tribal names was suggested. In particular, the subfamily Toddalioidae was broken up altogether and its former members were rearranged among several of the 17 provisional tribes within the subfamily Rutoideae s. lat.

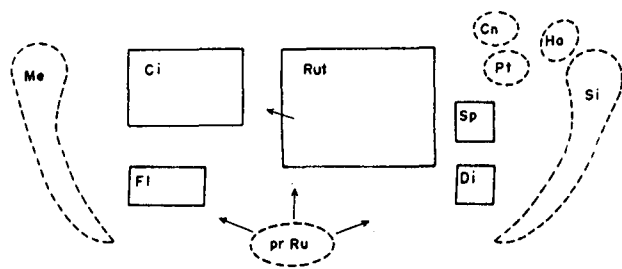


Figure 1. A suggested phylogeny of the Rutales, based on the distribution of secondary metabolites, according to Waterman (---)⁶ and Silva et al (—)⁷, Me = Meliaceae, Ci = Citroideae, Fl = Flindersioideae, Ru = Rutoideae, Sp = Spathelioideae, Dic = Dictyolomatoideae, prRu = proto-Rutaceae genera, Cn = Cneoraceae, Pt = Pteroxylaceae, Ha = *Harrisonia* and Si = Simaroubaceae. The results of the present work provide firm support for including the subfamily Dictyolomatoideae near the allied taxa Spathelioideae, Pteroxylaceae, Cneoraceae and *Harrisonia*.

Phylogenetic progressions could be recognized from parallel changes of morphological characters and biosynthetic pathways to secondary metabolites. As a general trend, a stepwise replacement of benzylisoquinolines by simple and complex anthranilic acid derived alkaloids, and eventually by coumarins and/or limonoids was confirmed⁷.

By this criterion of evolutionary character replacement, Rutoideae is the basic subfamily of Rutaceae. Benzylisoqui-

noline alkaloids appear (in *Zanthoxylum*-tribe) and most significantly, ample diversification of quinolone alkaloids occur. Simple anthranilate alkaloids with coumarins and/or limonoids characterize other ancient evolutionary branches of the family, Aurantioideae, Flindersioideae and Spathelioideae. The sole known limonoid from Flindersioideae is similar to limonoids type, found in Meliaceae⁸. The alkaloids, limonoids³ and chromones that we have isolated from *D. vandellianum* are very closely related to those isolated from *S. sorbifolia* showing the chemical affinity between the subfamilies Spathelioideae and Dictyolomatoideae. Since chromones are otherwise unknown in the Rutaceae, *Spathelia* and *Dictyoloma* differ from the other "Rutaceae". In addition the chromones can also suggest relationships to the Pteroxylaceae, Cneoraceae and *Harrisonia abyssinica* (Simaroubaceae) (Fig. 1).

ISOLATION OF THE CONSTITUENTS

The roots of *D. vandellianum* were collected in the Instituto Agrônomico de São Paulo, and a voucher is deposited in the Herbarium of Instituto de Biociências – USP – São Paulo. The roots were ground and extracted with dichloromethane. Evaporation of the solvent yielded a gum which was chromatographed over silica gel column. Elution with CH₂Cl₂ containing increasing amounts of MeOH afforded after final purification on preparative TLC, 6-(3-methyl-but-2-enyl)-allopteroxylin (1)⁴ (80 mg) and sorbifolin (2)⁵ (90 mg).

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