

Article

Drimane-Type Sesquiterpenoids as Chemosystematic Markers of Canellaceae*

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Poligodial, isopoligodial, mukaadial, e poligonona foram isoladas pela primeira vez de *Capsicodendron dinisii*. O isolamento dessas substâncias pertencentes ao grupo de sesquiterpenos do tipo eudesmano, presentes em Canellaceae, permitiu estabelecer maior afinidade do gênero Sul-americano *Capsicodendron* com o gênero Africano *Warburgia* do que com o gênero *Cinnamosma* de Madagascar.

Polygodial, isopolygodial, mukaadial and polygonone were isolated for the first time from *Capsicodendron dinisii*. Thus, with respect to drimane-type sesquiterpenoids of the Canellaceae, the close affinity of the South American genus *Capsicodendron* with the African genus *Warburgia* rather than the Madagascarian genus *Cinnamosma* is established.

Keywords: dinisii, Capsicodendron, Warburgia, Cinnamosma, drimane sesquiterpenoids

Introduction

Stem bark of the South American arboreal species *Capsicodendron dinisii* (Schwacke) was reported to contain two cytotoxic compounds, cinnamodial (**1d**) and capsicodendrin (**1e**), besides three inactive compounds 6 β -acetoxyisodrimenin (**3a**), ugandensolide (**3b**) and futronolide (**3c**). The leaf-twig extract of the same species yielded another cytotoxic compound, cinnamosmolide (**4c**)¹.

Experimental

Isolation of the constituents

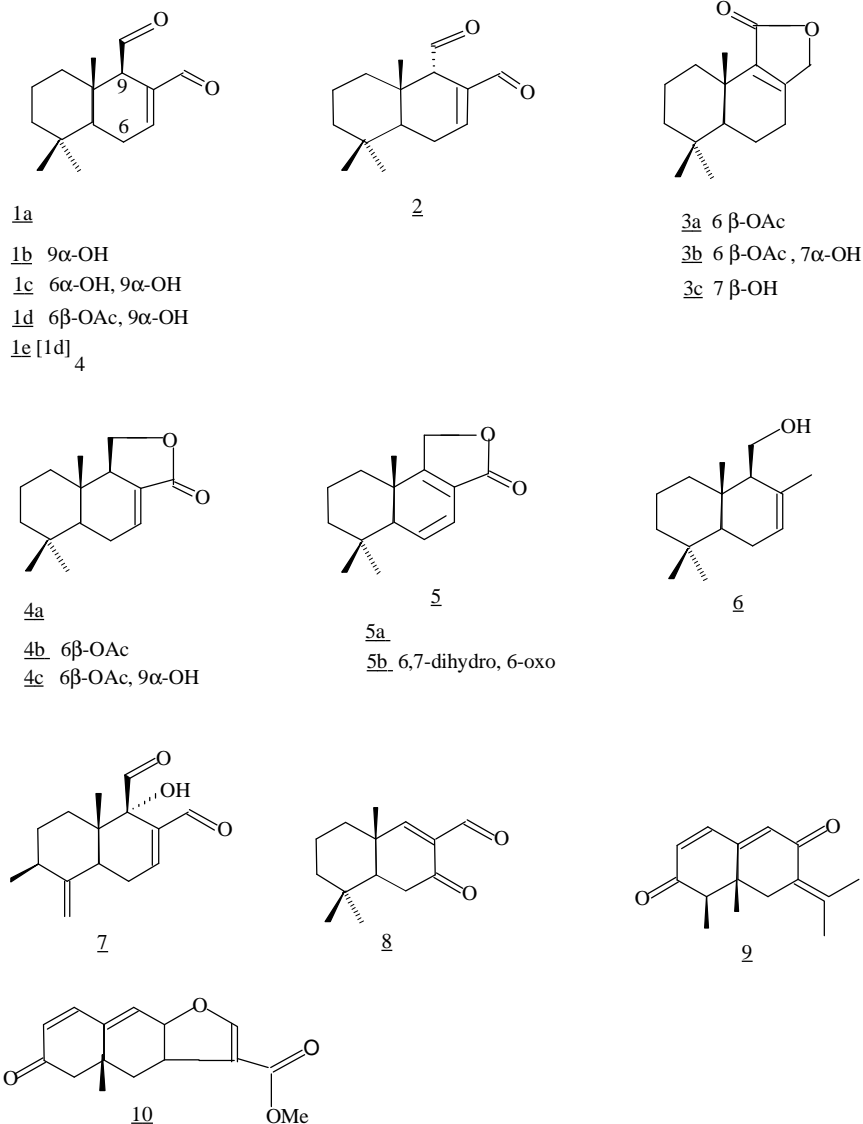
Capsicodendron dinisii was collected near Curitiba and identified by Dr. Gerdt Hatschbach (Herb. Museu Botânico Municipal, Curitiba). Dried, milled stem bark (2.5 kg) was extracted successively with C₆H₁₄ and EtOH. The solutions were filtered and evaporated to dryness, leading respectively to 61 and 250 g of extract. The C₆H₁₄-extract was

partitioned between C₆H₁₄ and MeOH-H₂O 19:1. Both solutions were evaporated to dryness, leading respectively to 18 and 38 g of residue. The latter partition fraction of the crude hexane extract was submitted to column chromatography (Si gel, 60 g). The following fractions were eluted with the indicated solvents: A (15 g, C₆H₁₄), B (11 g, CH₂Cl₂), C (7 g, AcOEt), D (4g, EtOH). Subsequent fractionation on column chromatography, preparative TLC (Si gel) and recrystallization led from A to **8** (23 mg), **2** (54 mg) and **1d** (14 mg); and from C to **1d** (800 mg), **1e** (tetramer of 1d, 55 mg) and **1c** (26 mg), in this order. **1d** (1 g) was obtained from B by cryst. from C₆H₁₄-Me₂CO. The mother liquor was evaporated to dryness. The residue (10 g), submitted to column chromatography and preparative TLC (Si gel) gave **1a** (83 mg).

Polygonone (**8**), yellow crystals, mp 123-135° (C₆H₁₄).
UV $\lambda_{\max}^{\text{MeOH}}$ nm: 237 (ϵ 7000).

¹H NMR (60 MHz, CDCl₃) δ : 0.90, 0.93, 1.30 (s, 3Me), 1.3-2.1 (m, 7H), 2.3-2.6 (m, 2H-6), 6.30 (s, H-9), 9.60 (s,

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CHO). $^{13}\text{C-NMR}$ (20 MHz, CDCl_3) δ : 18.1 (C-2, C-15), 21.0 (C-14), 32.4 (C-13), 33.0 (C-4), 34.0 (C-6), 38.3 (C-1, C-10), 40.8 (C-3), 50.4 (C-5), 137.7 (C-8), 163.1 (C-9), 193.8 (C-12), 200.8 (C-7). MS m/z (rel. int.): 220 $[\text{M}]^+$ (23), 205 $[\text{M-Me}]^+$ (6), 192 $[\text{M-CO}]^+$ (8), 191 $[\text{M-CHO}]^+$ (32), 177 $[\text{M-Me-CO}]^+$ (8), 163 (13), 149 (14), 138 (10), 135 (18), 124 (18), 123 (33), 121 (59), 109 (40), 107 (28), 105 (15), 41 (100).

Results and Discussion

During the present work a fresh sample of stem bark was collected from a tree in the vicinity of Curitiba, Paraná State. Fractionation of a hexane extract led to 1d and 1e, additionally to polygodial (1a), mukaadial (1c), isopolygodial (2) and polygonone (8). With the exception of 8 all other compounds have been found previously in other species of the family Canellaceae (Table 1). In each case

the identification, achieved by analysis of UV, IR, ^1H NMR, ^{13}C NMR and mass spectra, was confirmed by comparison of mp, specific rotation and with published data.

The nor-sesquiterpene polygonone (8) was mentioned previously twice in the literature. First as the oxidation product of polygodial, an isolate of *Polygonum hydropiper* (Polygonaceae², and subsequently as an authentic constituent of this species³. Nevertheless published data on this compound are restricted to the registry of two $^1\text{H-NMR}$ (60 MHz, CDCl_3) peaks (δ : 1.07, s, 9H; 10.36, s, CHO) and of some MS peaks (m/z : 220, 215, 192, 124, 109)³. For this reason more data are given in the Experimental of the present communication.

In addition to Canellaceae and Polygonaceae, Porellaceae³ and Winteraceae⁴ have been found to accumulate drimane-type sesquiterpenoids. Canellaceae and Winter-

Table 1. Distribution of drimane-type sesquiterpenoids in species of Canellaceae.

	<i>Capsicodendron dinisii</i>	Canella winterana	<i>Warburgia</i>		<i>Cinnamosma fragans</i>
			<i>stuhlmanii</i>	<i>W. ugandensis</i>	
Polygodial (1a)	*		+ (09)		
Warburganal (1b)			+ (10)	+ (05, 09, 10)	
Mukaadial (1c)	*		+ (11)	+ (11)	
Cinnamodial (1d)	* + (01)			+ (12, 09)	+ (13)
Capsicodendrina (1e)	* + (01)				
Isopolygodial (2)	*		+ (14)		
6 β -Acetoxyisodrimenin (3a)	+ (01)				
Ugandensolide (3b)	+ (01)			+ (12)	
Futronolide (3c)	+ (01)				
Cinnamolide (4a)			+ (09)	+ (09)	+ (13)
Bemarinolide (4b)					+ (15)
Cinnamosmolide (4c)	+ (01)				+ (13)
Bemadienolide (5a)			+ (09)	+ (09)	+ (15)
Fragolide (5b)					+ (15)
Trimenol (6)				+ (16)	
Muzigadial (7)		+ (18)		+ (05)	
Polygonone (8)	*				
Warburgiodione (9)				+ (16)	
Warburgin (10)				+ (16)	

* presence ascertained in present work;

+ presence reported in the literature; **1a** syn. tadeonal (18); **1d** syn. ugandensidial (12); **2** syn. epipolygodial (10); **7** syn. canellal (17); **8** and **9** are eremophilane-type sesquiterpenoids (12); non sesquiterpenoidal constituents of Canellaceae were reported for *Canella alba* (19), *Cinnamosma fragans* (19) and *C. madagascariensis* (15, 19, 08).

aceae both belong to the superorder Magnoliiflorae, albeit to different orders, respectively Annonales and Magnoliales⁵. However, Porellaceae belong to the class Hepaticae of the division Bryophyta and Polygonaceae, although angiosperms show morphologically and chemically (presence of gallotannins and ellagitannins) no close kinship with the magnolialean families (absence of such tannins)⁶.

Nevertheless within the Canellaceae drimanic compounds constitute a neat unifying theme. True only one of such sesquiterpenoids (**1d**) has so far been isolated from all three genera, *Capsicodendron*, *Warburgia* and *Cinnamosma*, but four drimanes (**1a**, **1c**, **2**, **3b**) are common to the first two genera, two (**4a**, **5a**) are common to the last two genera, one (**4c**) is common to the first and third genera and only one again (**7**) is common to *Warburgia* and a fourth genus, *Canella*. Hence, considering identity of chemical composition, *Capsicodendron* and *Warburgia* show the closest relationship, followed by the pair *Warburgia* and *Cinnamosma*, with *Capsicodendron* and *Cinnamosma* as well as *Warburgia* and *Canella* still less closely related. Analogous trends are observed counting

differences of compound composition. Both pairs, *Capsicodendron* and *Warburgia* as well as *Warburgia* and *Cinnamosma*, show ten differences, while the more distantly related *Capsicodendron* and *Cinnamosma* show 11 differences in drimane-type sesquiterpenoidal composition. From the morphological point of view the South American genera of Canellaceae are considered to be the most archaic⁷. Superposition of the chemical data on this postulate suggests a spacial radiation of the lineage to have taken place from tropical South American *Capsicodendron* in two directions, one towards the Caribbean *Canella* and the other over the tropical African *Warburgia* to the Madagascan *Cinnamosma*.

The occurrence of shikimate derivatives, including a quaternary aporphine⁸, as replacement characters of drimane-type sesquiterpenoids in *C. madagascariensis* is consistent with the general placement of the family Canellaceae in the Magnoliiflorae.

It is also important to point out that this is a particular class of sesquiterpene does not occur widely in nature. However, the majority of the publications in the literature

in the last decade does not report the presence of this class of compounds in terrestrial plants, but in sponges^{21, 22}, in the fern *Nephrolepis biserrata*²³, in *Polyporus articulatus*²⁴ and in the fungus *Aspergillus ustus* var. *Pseudodeflectus*²⁵.

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