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STRUCTURAL CONFIRMATION OF DIHYDROCINNAMIC ACIDS FROM *ADISCANTHUS FUSCIFLORUS* BY ^{13}C NMR*

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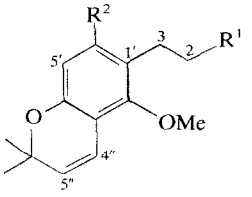
Key Word Index—*Adiscanthus fusciflorus*; Rutaceae; dihydrocinnamic acids; alkaloids; ^{13}C NMR spectra.

Abstract—In the wood of *Adiscanthus fusciflorus* six known alkaloids 4-methoxy-2-quinolone, 1-methyl-4-methoxy-2-quinolone, dictamine, skimmianine, γ-fagarine and *N*-methylflindersine and two new dihydrocinnamic acids 3-[2′,6′-dimethoxy-6″,6″-dimethylpyrano(2″,3″:4′,3′)phenyl]-propionic acid and its methyl ester were identified. The structures of the dihydrocinnamic acid derivatives were confirmed by ^{13}C NMR.

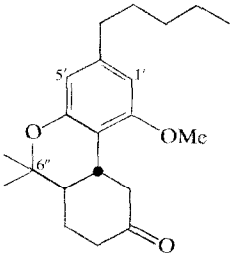
Adiscanthus fusciflorus Ducke, an arboreous Rutaceae species from the Amazon region, contains in a section of its trunk (bark included) 4-methoxy-2-quinolone, 1-methyl-4-methoxy-2-quinolone, dictamine and skimmianine [3], γ-fagarine [4] and *N*-methylflindersine. All these alkaloids have been separated previously from other rutaceous species, the first four inclusively from another Amazonian species, *Hortia longifolia* Spr. ex Engl. [3], and the last one by *N*-methylation of natural flindersine [5]. Their identification was based on spectra and direct comparison with authentic samples.

Two additional constituents, isolated from the same extract of *A. fusciflorus*, were the dihydrocinnamic acid derivatives **1a** and **1b**, which, jointly with dihydrocinnamyl alcohols such as **1c** [6], had been previously found in *Hortia badinii* M.A. Lisboa. The structural elucidation of these natural products had been based chiefly on the interpretation of ^{1}H NMR spectra. Their re-isolation was therefore an opportunity to test the proposed formulae by ^{13}C NMR.



1a $R^1 = CO_2Me$, $R^2 = OMe$
1b $R^1 = CO_2H$, $R^2 = OMe$
1c $R^1 = CH_2OH$, $R^2 = H$

The phloroglucinol type substitution for **1a** can be safely accepted from ^{1}H NMR evidence for the sole aromatic proton (δ 6.18). The corresponding unsubstituted C-5′ must indeed be vicinal to only one methoxyl (δ 55.3), ^{13}C NMR showing the other one (δ 62.0) to be flanked by two *ortho* substituents. The signals due to the corresponding *ipso*-carbons (C-6′ δ 158.5, C-2′ δ 154.9) can be easily assigned due to their complex secondary splitting in the fully proton-coupled C spectrum. In this same spectrum, signals of the *ipso*-carbons C-2″ and C-3″ show a contrastingly simpler splitting pattern which can be eliminated by decoupling respectively at the resonance frequencies of H-4″ (double irradiation at δ 6.48) and H-5″ (double irradiation at δ 5.45). These decoupling experiments were additionally very useful in the confirmation of the respective assignment of signals to C-4″ and C-5″ since the first order C—H couplings are eliminated. Finally, double irradiation at the frequency of the gem-dimethyl protons (δ 1.38) collapsed the fine splitting of the C-5″ signal, confirming the vicinality of this carbon and CMe_2. At this stage, since correlation of signals to carbons of the propionic acid moiety is trivial, only the signals at δ 113.7 and 75.5 remained to be assigned, a task performed by comparison with model compounds **2** [7] and **3** [8], respectively.



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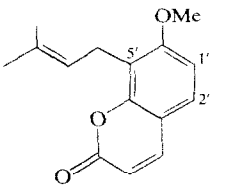

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The spectrum of **1a** served as the basis in the interpretation of the spectra of **1b**, dihydro-**1b** and **1c**. The suppression of the 4″,5″-double bond of **1b** in dihydro-**1b** caused a paramagnetic shift of the C-2″ signal (Δδ 4.4), an expression of the endocyclic homoallylic effect [9]. Most significantly, from the

* Part IV in the series "The Chemistry of Brazilian Rutaceae". For Part III see ref. [1]. Based on part of the M.S. thesis presented by P.C.V. to Universidade de São Paulo (1978). Also part of a project on the ^{13}C NMR spectroscopy of natural products. For the preceding paper see ref. [2].

Table 1. Carbon shifts of the natural dihydrocinnamic acids and dihydro derivative **1**, and the model compounds **2** and **3***

C	**1a**	**1b**	Dihydro-**1b**	**1c**	**2**[7]	**3**[8]
MeO-1	51.2					
1	173.5	176.5	179.5	61.4		
2	34.0	33.8	34.2	33.5		
3	19.0	18.7	19.0	24.9		
1′	113.7	113.5	113.0	125.7		
2′	154.9	154.4	153.4	153.4	158.1	
MeO-2′	62.0	61.8	60.6	62.1		
3′	107.4	107.2	106.5	114.4	109.7	117.6
4′	152.9	152.5	156.9†	152.0	153.9	152.5
5′	95.7	95.6	96.0	112.5	109.9	112.5
6′	158.5	158.2	157.2†	130.2		159.9
MeO-6′	55.3	55.0	55.3			
4″	117.2	116.7	17.1	117.1		
5″	126.7	126.7	32.5	126.9		
6″	75.5	75.6	74.1	75.4	76.3	
2Me-6″	27.7	27.6	26.7	27.6	27.8 18.6	

* The numbering system of the model compounds was selected to facilitate comparison of analogous carbons in **1**, **2** and **3**.
† Interchangeable.

point of view of structural confirmations, the C-6′ (δ 158.5) and C-3′ (δ 19.0) peaks of **1a** appear at higher (δ 130.2) and lower (δ 24.9) field, respectively, in the spectrum of **1c**. This is due to the absence in this compound of MeO-6′ which thus fails to shield C-3 through a γ-effect.

EXPERIMENTAL

Isolation of the constituents. Adiscanthus fusciflorus Ducke was collected near Manaus, AM and identified by W. A. Rodrigues, botanist, Instituto Nacional de Pesquisas da Amazônia. Powdered trunkwood and bark (2 kg) were extracted with EtOH. The extract (20 g) was suspended in hexane, filtered, the hexane evapd and the residue (7 g) submitted to dry column chromatography (Si gel deactivated with 10% H_2O, C_6H_6–$CHCl_3$, 9:1). The column was extruded and divided into 8 equal parts which gave from bottom to top 8 fractions. Fraction 4 was purified by TLC (Si gel, C_6H_6–EtOAc, 7:3) giving **1a** (30 mg). Fractions 5 and 6 were washed with hexane to give **1b** (200 mg). Fraction 7 contained 1-methyl-4-methoxy-2-quinolone. The hexane insol. part of the extract was suspended in $CHCl_3$ and filtered. The $CHCl_3$ was evapd and the residue (6 g) submitted to Si gel (120 g) column chromatography, elution with $CHCl_3$–MeOH, 100:0 to 95:5, giving fractions A to G. Fraction B was purified by TLC (Si gel, C_6H_6–EtOAc, 4:1) to give **1a** (60 mg). Fraction C was separated by TLC (Si gel, C_6H_6–EtOAc, 7:3) into dictamine (20 mg) and γ-fagarine (60 mg). Fraction D was purified similarly to give *N*-methylflindersine (50 mg). Fraction E was separated by TLC (Si gel, C_6H_6–EtOAc, 3:2) into skimmianine (20 mg) and 1-methyl-4-methoxy-2-quinolone. Fraction G was washed and cryst. from EtOH to give 4-methoxy-2-quinolone. Fractions A and F did not lead to pure compounds.

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