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Article

Dibenzylbutyrolactone Lignans and Coumarins from *Ipomoea cairica*[*]

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Das partes aéreas de *Ipomoea cairica* (L.) Sweet (Convolvulaceae) foram isolados as cumarinas umbeliferona e escopoletina, as lignanas dibenzil-γ-butirolactonas arctigenina, matairesinol e traquelogenina, além de β-sitosterol e ácidos graxos. A análise dos espectros de RMN ^{13}C permitiu revisar alguns deslocamentos químicos descritos na literatura para estes e outros lignóides.

From the aerial parts of *Ipomoea cairica* (L.) Sweet (Convolvulaceae) the coumarins umbelliferone and scopoletin, and the dibenzyl-γ-butyrolactone lignans arctigenin, matairesinol and trachelogenin, were isolated along with β-sitoterol and fatty acids. The analysis of the RMN ^{13}C spectra of these and other lignoids described in the literature made it possible to revise some chemical shift assignments.

Keywords: *Ipomoea cairica, Convolvulaceae, coumarins, dibenzylbutyrolactone lignans, ^{13}C-NMR* data

Introduction

Ipomoea cairica, Convolvulaceae family, is a climbing plant growing in Bahia, Rio de Janeiro, Paraná, and probably in other Brazilian states[1]. Hexane and methanol extracts of the dried aerial parts of a specimen of this plant afforded three lignoids (**1-3**) and two coumarins (**4** and **5**), along with palmitic and stearic acids and β-sitosterol. Lignoids **1-3** and the two coumarins have been previously reported. Earlier chemical investigations of the Convolvulaceae family did not report the occurrence of lignoids[2], except for pinoresinol dimethyl ether isolated from *Humbertia madagascariensis*[3]. The nomenclature and numbering of compounds **1-3** follow the rules outlined in a recent review[4].

Results and Discussion

The aqueous methanol extract of a specimen of Ipomoea cairica was extracted successively with chloroform and *n*-butanol. The separation of lignoids **1-3** and coumarins **4** and **5** was achieved by chromatography on an alumina column and silica gel preparative thin layer chromatography of the chloroform extract. Compounds **1-5** have been previously reported. Lignoid **1** has been isolated from *Arctium lappa* (Compositae)[5], *Forsythia xoreana*, and F. *viridissima* (Oleaceae)[2], **2** from *Stellera chamaejasme* (Thymelaeaceae), *Tsuga chinensis* (Pinaceae), *F. xorena*, and *F. viridissima* (Oleaceae)[2], and **3** from *Trachelospermum asiaticum* (Apocynaceae) [6]. Coumarins umbelliferone (**4**) and scopoletin (**5**) have been recorded in several species of the Convolvulaceae family. Scopoletin appears in *Ipomoea batatas* as a phytoalexin[7,8].

During the course of our analysis of the ^{13}C-NMR spectra of compound **1** and the mixture of **2** and **3** it was noted that some chemical shift assignments recently published for these and other lignoids[9,10] required revision (Table 1).

As anticipated, the comparison of the chemical shifts of the carbon atoms of lignoid **7** with those of the 9'-oxo compound (*e.g.* **6**) clearly showed a γ-effect at C-7' due to the introduction of the carbonyl oxygen at C-9' (Table 1). Thus,

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[*] Based in part on the M.Sc. thesis submitted by O.O. de A.L. to the Universidade Federal Rural do Rio de Janeiro, Seropédica, Rio de Janeiro - RJ, Brazil (1989).

Table 1. ^{13}C NMR spectral data for Lignoids **1-3** isolated from *Ipomoea cairica* compared with **6**, **7**[9], and **8**[10] *.

C	**1**	**2**	**2+3**	**3**^{b}		**6**^{b}		**7**	**8**^{b}	
1	130.30	-	130.89	-	(131.10)	130.80	(130.80)	132.90	132.10	(127.74)
2	111.18^a	-	111.41	-	(111.60)	111.80	(114.50)	113.20	108.36	(109.16)
3	148.57	-	148.97	-	(146.60)	149.30	(148.18)	148.30	147.86	(147.86)
4	146.56	146.58	-	146.45	(149.20)	147.10	(147.10)	145.70	146.99	(147.86)
5	111.44^a	-	112.14	-	(112.80)	112.00	(111.80)	115.60	109.16	(108.36)
6	120.46	120.70	-	121.17	(120.90)	120.80	(120.80)	121.90	121.83	(121.83)
7	38.14	38.28	-	31.51	(31.60)	38.20	(34.60)	39.80	31.74	(43.97)
8	40.90	40.98	-	43.76	(43.80)	41.10	(41.10)	47.10	43.97	(31.74)
9	71.24	71.26	-	70.10	(70.20)	71.40	(71.40)	73.50	69.97	(69.97)
1’	129.33	129.40	-	125.99	(126.20)	129.60	(129.60)	132.90	127.74	(132.10)
2’	111.65^a	-	112.63	-	(112.30)	112.30	(112.30	113.20	108.42	(110.55)
3’	147.66	-	147.68	-	(145.10)	148.10	(149.30)	148.30	147.86	(146.99)
4’	144.38	144.38	-	144.90	(147.90)	144.90	(144.90)	145.70	146.99	(146.99)
5’	114.03	114.04	-	114.23	(114.40)	114.50	(112.00)	115.60	110.55	(108.42)
6’	121.96	121.92	-	123.03	(123.20)	122.10	(122.10)	121.90	123.39	(123.39)
7’	34.51	34.59	-	42.02	(42.00)	34.60	(38.20)	39.80	42.24	(42.24)
8’	46.57	46.54	-	76.35	(76.50)	46.70	(46.70)	47.10	76.27	(76.27)
9’	178.57	-	178.27	-	(178.60)	179.00	(179.00)	73.50	178.19	(178.19)
OMe	55.77	-	55.88	-	(55.90)	55.90	(55.90)	-	-	-
OCH_2O	-	-	-	-	-	-	-	-	101.10	(101.10)
	-	-	-	-	-	-	-	-	100.98	(100.98)

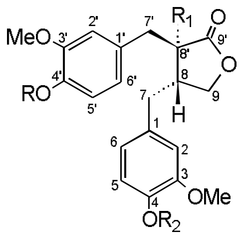
* The spectra were recorded in $CDCl_3$ (**1** -**3**, **6**, and **8**) and $D_2O + CD_3COCD_3$ (**7**), chemical shifts on the δ (ppm) scale with TMS as int. standard;
^{a} Signals with same letter may be interchangeable in each vertical column.
^{b} Values given in parentheses are the reported chemical shifts of corresponding compounds as described in the literature[9,10].

some assignments have been revised for the non-aromatic carbon atoms of compounds **6**[9] and **8**[10] (Table 1). The chemical shifts for the aromatic carbon C-5 (methine *ortho* to the methoxyl group) and C-5’ (methine *ortho* to the hydroxyl group) in lignoids **1** and **3** were distinguished on the basis of the γ-effect of the methyl of the 3-OMe group (*e.g.* **9-11**)[11]. Model compounds **9-11** may also be used to demonstrate the known shielding effects induced by OH and OMe groups in the *para* and *ortho* positions, and the deshielding effect on the *ipso*-carbon by methylation. The oxygen atom of the hydroxyl group at C-8’ is responsible for an upfield shift of the C-1’ and C-7 (γ-effect).

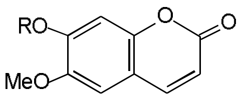
Conclusions

Convolvulaceae is a large family comprising about 59 genera and more than 1800 species, which are found in tropical and subtropical regions as herbs, climbers, or shrubs[12]. The natural products reported in the species of this family may be classified as polyketides, terpenoids (mono-, sesqui-, di-, and triterpenoids), steroids, shikimides (coumarins and benzoic and cinnamic acid derivatives), flavonoids (flavonols, anthocyanins, flavones, flavanones), one xanthone (mangiferin), alkaloids (pyrrolidines, tropanes, indolizidines, and ergolines), and other compounds. To the best of our knowledge, lignoids such as **1-3** have been hitherto unreported as natural products of the Convolvulaceae family, with the exception of pinoresinol dimethyl ether (**12**) which has been isolated from *Humbertia madagascariensis*[3]. The fact that umbelliferone (**4**) was isolated points to the possibility that the specimen used in our investigation had been infested by a fungus, since this substance was recently found to be a phytoalexin in *I. batatas*[7,8]. Moreover, it can be assumed that lignoids were also biosynthesized as phytoalexins. At the ecological level, there is evidence that lignans play a role in plant-plant, plant-fungus, and plant-insect interactions[13].

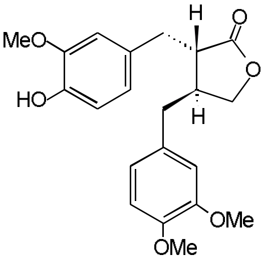
Matairesinol (**2**), formed via the coupling of two phenylpropane units having the ferulic substitution pattern, would be a logical precursor of the other lignoids **1** and **3** through methylation of the hydroxyl group localized at C-4’[14].



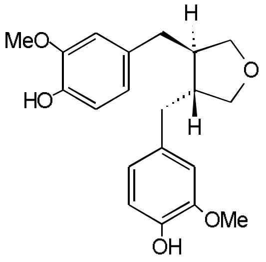
1 R=R$_1$=H, R$_2$=Me
1a R=Ac, R$_1$=H, R$_2$=Me
2 R=R$_1$=R$_2$=H
2a R=R$_2$=Me, R$_1$=H
3 R=H, R$_1$=OH, R$_2$=Me



4 R=Me
5 R=H



6



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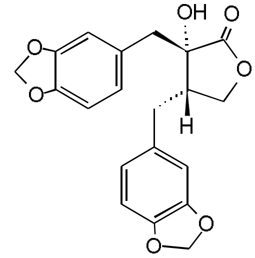

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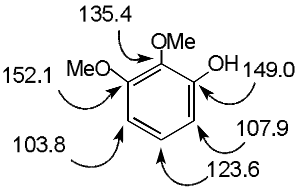

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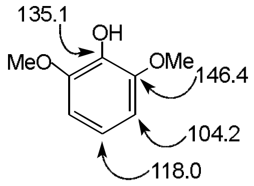

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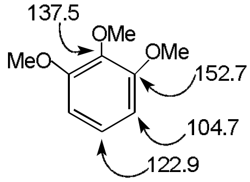

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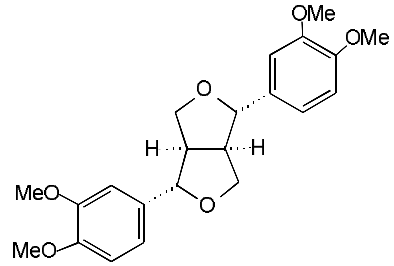

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Phytochemical studies of other specimens of *Ipomoea cairica* have also revealed the presence of the lignanolides arctigenin **1** and trachelogenin **3** in an aqueous methanol extract[15]. That investigation was probably developed during the same period as our study of the same species.

Experimental

General

Mps are uncorrected. NMR (^{1}H: 100 and 200 MHz; ^{13}C: 25.2 and 50.3 MHz) spectra were recorded in a $CDCl_3$ solution with TMS as the internal standard. EIMS were measured by direct inlet at 70 eV ionization. GC/MS spectra were measured on a GCHR/MS-C 5987A (HP) spectrometer, using a capillary glass column (OV-1701; 20 m).

Plant material

The plant material of *Ipomoea cairica* (L.) Sweet, Convolvulaceae family, was collected on the campus of the Universidade Federal do Rio de Janeiro, Rio de Janeiro, Brazil. The specimen was identified by Rosa Fuks, Jardim

Botânico do Rio de Janeiro (voucher specimen nº 257337), Rio de Janeiro, Brazil.

Isolation of the constituents

Dried and milled whole plant (1.35 kg) was extracted at room temperature with hexane and then with MeOH. A portion (1 g) of the residue obtained from the hexane extract (98 g) was dissolved in ether and treated with aqueous 10% $NaHCO_3$. After neutralization and extraction with ether, the aqueous solution gave a mixture of fatty acids (60 mg). The remaining residue (97 g) was dissolved in hexane and filtered on a $CaCO_3$ column to eliminate chlorophyll. The hexane solution was concd. *in vacuo* and the residue was submitted to silica gel column chromatography. Elution with hexane and hexane-EtOAc (9:1) gave aliphatic material and β-sitosterol, respectively.

A portion (50 g) of the MeOH extract (250 g) was treated with tartaric acid 1% aqueous solution and successively extracted with $CHCl_3$ and n-BuOH. The $CHCl_3$ solution was concd *in vacuo* and a portion of the residue (300 mg) was chromatographed on a basic alumina (V) column. Elution with $CHCl_3$, $CHCl_3$-MeOH (mixts of the indicated composition), and MeOH furnished frs 1-6 ($CHCl_3$), 7 (99:1), 8 (95:5), 9 (1:1), and 10 (MeOH). Preparative TLC of fr-2 [silica gel GF-254, $CHCl_3$-MeOH (99:1)] and crystallization from MeOH-ether yielded arctigenin (**1**, 20 mg), mp 98-100 °C. The frs 3-6 were submitted to preparative TLC (silica gel H) with $CHCl_3$-MeOH (1:1), affording matairesinol (**2**) + trachelogenin (**3**). This mixture was identified by ^{13}C-NMR spectra (full decoupled and SFORD), and the purification of the individual compounds was achieved by preparative TLC (silica gel H) with MeOH. The less polar spot gave matairesinol (2,5 mg), mp 117-119 °C, after crystallization from MeOH; the more polar band was crystallized from MeOH to furnish trachelogenin (3,10 mg), mp 139-141 °C. Preparative TLC of fr-7 [silica gel H, $CHCl_3$-MeOH (99:1)] gave umbelliferone (**4**) and scopoletin (**5**).

Identification

The known compounds **1**[5], **2**, **3**[2], **4**[15], and **5**[16] were identified by comparison with authentic samples (**2-5**) and by spectral data, including derivatives obtained by acetylation (**1a**) with Ac_2O/Py and methylation (**2a**) with CH_2N_2/ether. The fatty acids mixture was methylated with CH_2N_2/ether, and the methyl esters of palmitic and stearic acids were identified by GC/MS.

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