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Article

Alkaloids from *Annona dioica*

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Do extrato etanólico da madeira de *Annona dióica* foram isoladas as conhecidas 1-aza-4-metilantraquinona, lasiodiplodina, liriodenina, uma mistura de 1-aza-5,9,10-trimetoxi-4-metil-2-oxo-1,2-diidroantraceno e 1-aza-8,9,10-trimetoxi-4-metil-2-oxo-1,2-diidroantraceno (geovanina) e o novo alcalóide 1,2-metilenodioxi-6α,7-desidroaporfina-4(*S*)-(4-hidroxi-3,5-dimetoxifenil)-3,4-diidro-2(1*H*)-piridinona. As estruturas destes produtos naturais foram elucidadas com base em seus dados espectrais, inclusive experiências de NOE e espectros de RMN 2D de correlação homonuclear ^{1}H-^{1}H-COSY e heteronuclear ^{1}H-^{13}C-COSY-$^{n}J_{CH}$ (HMQC, n=1 e HMBC, n=2 e 3).

From the ethanolic extract of the wood of *Annona dioica* were isolated the known 1-aza-4-methylanthraquinone, lasiodiplodin, liriodenine, a mixture of 1-aza-5,9,10-trimethoxy-4-methyl-2-oxo-1,2-dihydroanthracene and 1-aza-8,9,10-trimethoxy-4-methyl-2-oxo-1,2-dihydroanthracene (geovanine) and the new alkaloid 1,2-methylenedioxy-6α,7-dehydroaporphine-4(*S*)-(4-hydroxy-3,5-dimethoxyphenyl)-3,4-dihydro-2(1*H*)-pyridinone. The structures of these natural products were elucidated on the basis of their spectral data, including NOE experiments and homonuclear ^{1}H-^{1}H-COSY e heteronuclear ^{1}H-^{13}C-COSY-$^{n}J_{CH}$ (HMQC, n=1 and HMBC, n=2 and 3) 2D-shift-correlated NMR spectra.

Keywords: *Annona dioica*, Annonaceae, quinoline alkaloids, lignoaporphine, lasiodiplodin

Introduction

Annona dioica, Annonaceae, is a shrub distributed throughout the States of São Paulo, Minas Gerais, Paraná and Mato Grosso, Brazil, commonly called "ceraticum (do campo, or grande)", "arixicum" and "ariticum". The fruits and leaves are used against rheumatism and the seeds to heal diarrhea.[1]

This paper reports the isolation of the known 1-aza-4-methylanthraquinone (**1**), lasiodiplodin (**2**), liriodenine (**3**), along with a mixture of 1-aza-8,9,10-trimethoxy-4-methyl-2-oxo-1,2-dihydroanthracene (**4**, geovanine) and 1-aza-5,9,10-trimethoxy-4-methyl-2-oxo-1,2-dihydroanthracene (**5**), and the new alkaloid 1,2-methylenedioxy-6α,7-dehydroaporphine-4(*S*)-(4-hydroxy-3,5-dimethoxyphenyl)-3,4-dihydro-2(1*H*)-pyridinone (**6**). The structures were established by spectral analysis, mainly ^{1}H and ^{13}C NMR including homonuclear 2D ^{1}H-^{1}H-COSY and heteronuclear 2D ^{1}H-^{13}C-COSY-$^{n}J_{CH}$ (HMQC, n=1 and HMBC, n=2 and 3) and NOE experiments.

To the best of our knowledge, the compound **6** is hitherto unreported in the literature.

Results and Discussion

Comparative analysis of HBBD- and DEPT-^{13}C NMR spectra of each natural product (**1** to **6**) was used to identify signals corresponding to quaternary, methine, methylene and methyl carbon atoms. Compound **1** was previously isolated from *Cleistopholis patens*,[2,3] **2** from *Lasiodiplodia theobromae*[4] and *Euphorbia splendens*,[5] **3** from *Atherosperma moschatum*, *Liriodendron tulipifera*,[6] *Fusea longifolia*, *Siparuna guianensis,*[7] *Thalictrum sessile*[8] and many other plants species, and **4** (geovanine) from *Annona ambotay*.[9] The structural identification of these compounds was based on their spectral data, including homonuclear 2D ^{1}H-^{1}H-COSY and heteronuclear 2D ^{13}C-^{1}H-COSY-$^{n}J_{CH}$

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(n=1; n=2 and 3, COLOC) experiments and differential NOE data, together with comparison with literature values of ^{1}H and ^{13}C NMR (*vide supra*).

The mixture of **4** and **5** showed IR absorption for conjugated carbonyl function (ν_{max} 1650 cm^{-1}) and aromatic ring (ν_{max} 1560 and 1520 cm^{-1}). The multiplicity of each carbon signal of the two components **4** and **5** was deduced by comparative analysis of the HBBD- and DEPT-^{13}C NMR spectra (Table 1). This analysis in combination with GC-EIMS {Rt=2.41min (40%): *m/z* 299 ([M]$^+$ of **5**, 65%; Rt=3.08 min (60%): *m/z* 299 ([M]$^+$ of **4**, 63%)} and 1D ^{1}H and 2D ^{1}H-^{1}H-COSY NMR spectra (Table 1) allowed the deduction of the same molecular formula $C_{17}H_{17}NO_4$ for **4** and **5**. Comparison of ^{1}H NMR spectral data of **4** and of geovanine (isolated from *Annona ambotay*[9]) was used to characterize it as the same compound (Table 1) and consequently to establish the structure of **4** as 1-aza-8,9,10-trimethoxy-4-methyl-2-oxo-1,2-dihydroanthracene. This structure was confirmed by NOE difference experiments performed with irradiation at MeO-10 (δ_H 3.90) which resulted in signal enhancements at δ_H 2.75 (Me-4) and 7.75 (H-5) and irradiation at MeO-8 (δ_H 4.02) which showed NOE at δ_H 6.88 (H-7). The remaining signals observed in the ^{1}H (δ_H 7.82, t, *J* 8.2 Hz, H-7, position conjugated with carbonyl group; partial superimposition with signal at 7.75 of the H-5 of **4**), 6.59 (s, H-3), 2.65 (s, Me-4), 4.04 (s, MeO)] and ^{13}C (δ_C 63.79, MeO)] NMR and GC/MS (*vide supra*) spectra were speculatively used to propose the structure **5** (1-aza-5,9,10-trimethoxy-4-methyl-2-oxo-1,2-dihydroanthracene) for the other component present in the mixture, probably a new alkaloid.

Table 1. ^{1}H (200 MHz) and ^{13}C (50 MHz) NMR for **4**, in $CDCl_3$ and TMS as internal standard, compared with geovanine in $CDCl_3$.[9] Chemical shifts in δ (δ_H and δ_C) and coupling constants (*J*, in parenthesis)

	4[a] ^{13}C-^{1}H-COSY-$^1J_{CH}$		Geovanine (**4**)[9]
	δ_C	δ_H	δ_H
C			-
2	161.82	-	-
4	148.48	-	-
4a	114.27	-	-
8	155.27	-	-
8a	117.25	-	-
9	151.08	-	-
9a	129.02	-	-
10	136.53	-	-
10a	126.85	-	-
CH			
3	123.36	6.45 (s)	6.48 (s)
5	115.87	7.75 (d, 8.8)	7.77 (d, 8.0)
6	124.68	7.32 (t, 8.8)	7.35 (t, 8.0)
7	106.79	6.88 (d, 8.8)	6.91 (d, 8.0)
CH$_3$			
Me-4	23.22	2.75 (s)	2.78 (s)
MeO-8	56.16	4.02 (s)	4.04 (s)
MeO-9	62.70	3.88 (s)	3.93 (s)
MeO-10	62.70	3.90 (s)	3.91 (s)

[a] Number of hydrogen bound to carbon atoms deduced by comparative analysis of HBBD- and DEPT-^{13}C NMR spectra. Homonuclear 2D ^{1}H-^{1}H-COSY spectrum and {^{1}H}-^{1}H-NOE difference spectra were also used in these assignments. Chemical shifts (δ_H) and coupling constants (*J*) of hydrogen atoms deduced from 1D ^{1}H NMR spectrum.

The lignoaporphine alkaloid **6** showed IR absorption bands for a carbonyl group (ν_{max} 1660 cm^{-1}) and for aromatic ring (ν_{max} 1630, 1610, 1520 and 1500 cm^{-1}). The number of hydrogen atoms bound to each carbon atom was deduced by comparative analysis of the HBBD - (25 signals corresponding to 28 carbon atoms) and DEPT-^{13}CNMR (Table 2) in combination with ^{1}H NMR spectral data (1D and 2D ^{1}H-^{1}H-COSY) and low resolution mass spectrum (*m/z* 469 [M]$^+$, 100%, $C_{28}H_{23}NO_6$), allowing to establish the formula $(C)_{13}(C{=}O)(CH)_8(CH_2)_3(OCH_2O)(MeO)_2(OH) = C_{28}H_{23}O_6$ (455 daltons) + N = $C_{28}H_{23}NO_6$ (*m/z* 469, [M]$^+$). This molecular formula is compatible with an aporphine skeleton ($C_{16}H_9N$) sustaining one methylenedioxy group and one 4'-hydroxy-3',5'-dimethoxy-7',8'-dihydrocinnamoyl moiety in a lactam ring. In fact, the presence of this cinnamoyl system was evidenced by the chemical shifts of 2H-8' [δ_H 3.20 (dd, *J* 14.5; 6.2 Hz); 3.07 (br d, *J* 14.5 Hz)], H-7' [δ_H 4.80 (br d, *J* 6.2 Hz)], 2H-2',6' [δ_H 6.38 (*s*)] and 2MeO-3',5' [δ_H 3.74 (*s*)] in addition to the chemical shifts of C-1' (δ_C 131.77), 2CH-2',6' (δ_C 103.82), 2C-3',5' (δ_C 147.35), C-4' (δ_C 133.96), CH-7' (δ_C 37.96), CH_2-8' (δ_C 39.90) and C-9' (δ_C 167.65). The location of the cinnamoyl unit, involving carbon C-7 and the nitrogen atom, was defined by heteronuclear 2D ^{1}H-^{13}C long-range couplings ($^2J_{CH}$ and $^3J_{CH}$) between: C-7 (δ_C 115.85) and H-7' (δ_H 4.80, $^2J_{CH}$), 2H-8' (δ_H 3.20; 3.07, $^3J_{CH}$) and H-8 (δ_H 7.85, $^3J_{CH}$); C-6a (δ_C 132.22) and H-5 (δ_H 5.29, $^3J_{CH}$) and H-7' (δ_H 4.80, $^3J_{CH}$); C-9' (δ_C 167.65) and H-5 (δ_H 5.29, $^3J_{CH}$), H-7' (δ_H 4.80, $^3J_{CH}$) and 2H-8' (δ_H 3.20 and 3.07, $^2J_{CH}$). The remaining signals observed in the ^{1}H and ^{13}C NMR spectra (Table 2) were used to define the 2,3-methylenedioxyaporphine $[(C)_9(CH)_5(CH_2)_2(OCH_2O)]$ unit, being the homo- and heteronuclear correlations obtained from 2D ^{1}H-^{1}H-COSY and ^{1}H-^{13}C-COSY-$^nJ_{CH}$ (n=1, HMQC; n=2 and 3, HMBC) spectra summarized in Table 2. The 2D shift-correlated spectra were also used to complete ^{1}H and ^{13}C chemical shift assignments of **6**. The following cross-peaks observed in the NOESY spectrum were also utilized for additional confirmation of the structure proposed to **6**: a) NOE between H-8 (δ_H 7.85) and H-7' (δ_H 4.80) and 2H-

Table 2. ^{1}H (500 MHz) and ^{13}C (125 MHz) NMR spectral data of **6**, in $CDCl_3$ and TMS as internal standard. Chemical shifts in δ (δ_H and δ_C) and coupling constants (J, in parenthesis)[a]

	$^{1}Hx^{13}C$-HMQC-$^{1}J_{CH}$		$^{1}Hx^{13}C$-HMBC-$^{n}J_{CH}$		
	δ_C	δ_H	$^{2}J_{CH}$	$^{3}J_{CH}$	$^{1}Hx^{1}H$-NOE
C					
1	142.42	-		H-3; OCH_2O	
1a	117.17	-		H-11	
1b	117.07	-		H-3	
2	145.79	-	H-3	OCH_2O	
3a	126.97	-	H-4	H-5	
6a	132.22	-		H-5; H-7'	
7	115.85	-	H-7'	H-8; 2H-8'	
7a	130.34	-		H-7'	
11a	126.09	-		H-8	
1'	131.77	-	2H-2',6'; H-7'	2H-8'	
3',5'	147.35	-	2H-2',6'	2MeO-3',5'	
4'	133.96	-		2H-2',6'	
9'	167.65	-	2H-8'	H-5; H-7'	
CH					
3	108.82	7.13 (s)			
8	122.99	7.85 (d, 8.7)		H-10	
9	127.70	7.55		H-11	
10	125.09	7.54			
11	127.55	9.14 (dd, 8.0, 1.9)		H-9	
2',6'	103.82	6.38 (s)		H-7'	2MeO-3',5'; H-7'
7'	37.96	4.80 (d, 6.2)	2H-8'	2H-2',6'	H-8; 2H-2',6'
CH_2					
4	29.93	3.32 (dt, 15.8, 3.8) 3.19	H-5	H-3	
5	38.41	5.29 (dd, 12.3, 3.8) 3.11 (dt, 12.3, 2.8)	H-4		
8'	39.90	3.20 (dd, 14.5, 6.2) 3.07 (br d, 14.5)	H-7'		
OCH_2O	101.43	6.32 (br s) 6.31 (br s)			
CH_3					
2MeO-3',5'	56.27	3.74 (s)			

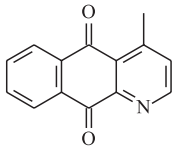
[a] Number of hydrogen bound to carbon atoms deduced by comparative analysis of HBBD- and DEPT-^{13}C NMR spectra. Superimposed ^{1}H signals are described without multiplicity and chemical shifts were deduced by ^{1}H-^{13}C-COSY-$^{n}J_{CH}$ (n=1, HMQC; n=2 and 3, HMBC) NMR spectra. Homonuclear 2D ^{1}H-^{1}H-COSY spectrum was also used in these assignments. Chemical shifts (δ_H) and coupling constants (J) of hydrogen atoms deduced from 1D ^{1}H NMR spectrum.

2',6' (δ_H 6.38); b) NOE between H-7' (δ_H 4.80) and 2H-2',6' (δ_H 6.38); c) NOE between 2H-2',6' (δ_H 6.38) and 2MeO-3',5' (δ_H 3.74); d) NOE between H-3 (δ_H 7.13) and pseudoequatorial H-4 (δ_H 3.19).

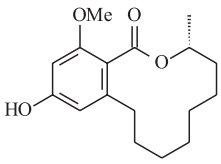
Additional peaks observed in the low resolution EIMS at *m/z* 316 (96%), 314 (22%) and 286 (26%) attributed to fragments **6a**, **6b** and **6c**, respectively, are also consistent with structure **6**.

Thus, the structure of the new lignoaporphine alkaloid **6** was established as 1,2-methylenedioxy-6a,7-dehydro-aporphine-4-(4-hydroxy-3,5-dimethoxyphenyl)-3,4-dihydro-2(1*H*)-pyridinone. The $[\alpha]_D$ of + 326° ($CHCl_3$; *c* 2.50) indicated that it was not a racemic mixture, ruling out the possibility of **6** being an artifact. The assignment of the absolute stereochemistry at the chiral centre CH-7' of the 3-(4-hydroxy-3,5-dimethoxyphenyl)propanoyl moiety of **6** was postulated by comparison of its optical rotation $[\alpha]_D$ + 326° ($CHCl_3$; *c* 2.50) with those reported for structures **7**-**10**, which contain an asymmetric carbon with nearly identical substituents. In those compounds the *S* configuration gave an optical rotation about 200° higher than the *R* configuration.[10] Consequently, the $[\alpha]_D$ + 326° ($CHCl_3$; *c* 2.50) is consistent with (*S*)-stereochemistry of the chiral carbon CH-7' present in the 3-(4-hydroxy-3,5-dimethoxyphenyl)propanoyl unit of **6**.

Thus, the structure of new lignoaporphine alkaloid was established as 1,2-methylenedioxy-6α,7-dehydro-aporphine-4(*S*)-(4-hydroxy-3,5-dimethoxyphenyl)-3,4-dihydro-2(1*H*)-pyridinone, IUPAC name 5-(4-hydroxy-3,5-methoxyphenyl)-(5*S*)-6,7,9,10-tetrahydro-5*H*-benzo[*g*][1,3]dioxolo[4',5':4,5]benzo[*de*]pyrido[3,2,1-*ij*]quinolin-7-one (**6**).



1



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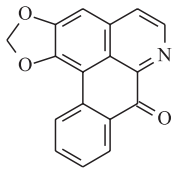

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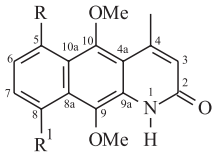
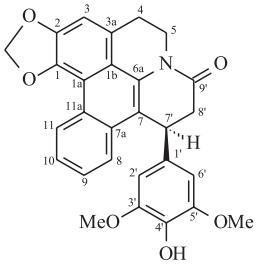
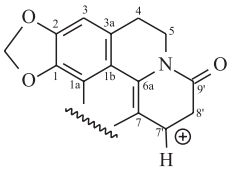


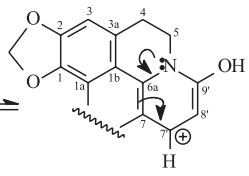
4 R=H, R^1=OMe
5 R=OMe, R^1=H

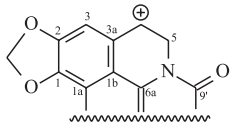


6

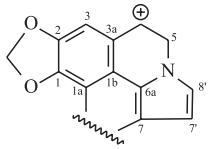


$C_{20}H_{14}NO_3$
6a, *m/z* 316 (96 %)

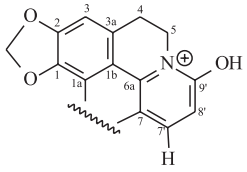


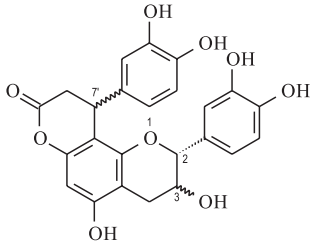


$C_{20}H_{12}NO_3$
6b, *m/z* 314 (22 %)



$C_{19}H_{12}NO_2$
6c, *m/z* 286 (26 %)





7 3α-OH, 7'β-Ar: $[\alpha]_D$ + 16^0 (Me_2CO, *c* 0.13)
8 3α-OH, 7'α-Ar: $[\alpha]_D$ - 192^0 (Me_2CO, *c* 0.14)
9 3β-OH, 7'β-Ar: $[\alpha]_D$ + 6.5^0 (MeOH, *c* 0.15)
10 3β-OH, 7'α-Ar: $[\alpha]_D$ - 107^0 (Me_2CO, *c* 0.10)

Experimental

General experimental procedures

Mps are uncorr. NMR spectra were run on Bruker AC-200 and Advance 500 spectrometers in $CDCl_3$ or CD_3COCD_3 using TMS as internal standard or by reference to the solvent signal ($CHCl_3$ at δ_H 7.24 or CD_2HCOCD_3 at δ_H 2.08 and $CDCl_3$ at δ_C 77.00 or CD_3COCD_3 at δ_C 24.8 and 206.0). EIMS were obtained at 70 eV on a Hewlett Packard spectrometer model 5987. The IR spectra were obtained on a Perkin-Elmer FT-1500 spectrometer. Column chromatography was carried out with silica gel 0.063–0.2 mm and TLC was done employing silica gel Kieselgel 60 from Merck and spots were visualized by UV (λ_{max} 259 and 360 nm) and exposure to I_2 vapour.

Plant material

A specimen of *Annona dioica* St. Hil. was collected in January 1990 at Serra da Moeda, Minas Gerais State, Brazil and identified by Professor José Badini of the Universidade Federal de Ouro Preto, Minas Gerais, where a voucher specimen is deposited.

Extraction and isolation of constituents

Dried and powdered wood (5.2 kg) was extracted successively with *n*-hexane and EtOH at room temp. and the solvent removed under vacuum to yield 81.79 g of residue. This residue was chromatographed on a silica gel column using CH_2Cl_2, $CHCl_3$, *n*-hexane-EtOAc (4:1, 3:2, 2:3 and 1:4), EtOAc and EtOAc-MeOH (4:1 and 1:1). Fractions 52-71, eluted with CH_2Cl_2, were rechromatographed on a silica gel column (70-230 mesh) using $CHCl_3$ and $CHCl_3$-MeOH (97:3) as eluents to furnish 15 fractions: fractions 6-10 yielded **1** (22 mg) and **2** (20 mg) after chromatography on a silica gel column using $CHCl_3$-MeOH (97:3). Preparative TLC ($CHCl_3$-MeOH, 97:3) of the fractions 98-115 (eluted with $CHCl_3$-MeOH 97:3) afforded **3** (15 mg) and **6** (83 mg). Fractions 135-229 (4.7 g, eluted with $CHCl_3$-MeOH 97:3) were chromatographed on a silica gel (100 g) column using CH_2Cl_2, CH_2Cl_2-$CHCl_3$ (1:1 and 1:4), $CHCl_3$, *n*-hexane-EtOAc (1:4) and MeOH to furnish **4+5** (18.8 mg) as amorphous yellow solid after treatment with acetone.

*1-Aza-4-methylanthraquinone (**1**).* Oil. Spectral data in agreement with literature values.[2,3]

*12-Hydroxy-14-methoxy-3-methyl-3,4,5,6,7,8,9,10-octahydro-1*H*-benzo[c]oxa-cyclododecin-1-one (**2**, Lasidioplodin).* Amorphous yellow solid, mp 183-186 °C; spectral data in agreement with lit. values.[4,5]

*8*H*-Benzo[*g*][1,3]dioxolo[4',5':4,5]benzo [*de*]quinolin-8-one (**3**, Liriodenine).* Amorphous yellow solid, mp 284-286 °C; spectral data in agreement with lit. values.[6-8]

*Mixture of 1-Aza-8,9,10-trimethoxy-4-methyl-2-oxo-1,2-dihydroanthracene (**4**, geovanine) and 1-aza-5,9,10-trimethoxy-4-methyl-2-oxo-1,2-dihydroanthracene (**5**).* Amorphous yellow solid, mp 189-191 °C; IR (KBr) ν_{max}/cm^{-1}: 1650 (C=O), 1560 and 1520 (aromatic ring); GC Rt = 2.418 (**5**)/3.086 (**4**) min; EIMS (rel. int., **4/5**) *m/z*: 299 ([M]$^+$, 63/65), 284 (M-Me$^-$, 100/100), 269 (M-CH_2O, 76/72), 268 (M-MeO, 7/7), 252 (M-CH_2O-OH, 9/9), 240 (M-MeO-C=O, 17/18); ^{1}H and ^{13}C NMR of **4**: Table 1.

*1,2-methylenedioxy-6α,7-dehydroaporphine-4(*S*)-(4-hydroxy-3,5-dimethoxyphenyl)-3,4-dihydro-2(1*H*)-pyridinone (**6**).* Amorphous yellow solid, mp 211-213 °C; IR (KBr) ν_{max}/cm^{-1}: 3600, 3500, 1660, 1630, 1610, 1520, 1500, 1260, 1050, 850, 720 cm^{-1}; ^{1}H and ^{13}C NMR: Table 2.

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