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^{1}H and ^{13}C NMR Data of the Alkaloids and Coumarins from *Conchocarpus* Species

Dados de RMN ^{1}H e ^{13}C dos Alcaloides e Cumarinas das Espécies de Conchocarpus

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The genus *Conchocarpus* comprises more than 50 species, distributed from Nicaragua to northern Bolivia and southern Brazil. This genus is part of the Rutaceae family, which contains a variety of classes of secondary metabolites, represented mainly by alkaloids and coumarins, which are considered the chemical markers of this family. Therefore, the objective of this review is to describe the data of ^{1}H and ^{13}C Nuclear Magnetic Resonance spectral analysis, from alkaloids and coumarins isolated from *Conchocarpus* species, to aid in the comparison of metabolites isolated in the future, and facilitating the identification of new compounds. The literature presented 51 alkaloids and 15 coumarins isolated in the genus *Conchocarpus*, however, Nuclear Magnetic Resonance data on all the compounds are not available.

Keywords: Alkaloids; coumarins; *Conchocarpus*; rutaceae; secondary metabolites; Nuclear Magnetic Resonance.

1. Introduction

Rutaceae is a plant family of great extension and variety, comprising approximately 2,040 species, subdivided into more than 150 genera. The species are found in tropical and subtropical regions of the planet, distributed with great representation in tropical America, Australia, and southern Africa.[1,2]

This family is recognized by the genus *Citrus*, the most popular among the genera, characterized by citrus fruits, such as oranges, lemons, and tangerines. The Rutaceae family also contains species that are sources of essential oils, in addition to representatives in the timber industry. Species can be found in the form of small bushes or even trees over 40 meters high.[1,3]

The diversity of Rutaceae expands to secondary metabolites, containing different classes, such as alkaloids, coumarins, flavonoids, terpenoids, and steroids, among others.[2] Therefore, this family is the target of research, since the phytochemical compounds of all plant genera have not yet been studied. Among them, the genus *Conchocarpus* attracts attention, for being the largest genus of the tribe Galipeeae and subtribe Galipeinae, containing 50 species, and with less than 15 works in the literature on the phytochemical isolation of the species.[4-6]

Conchocarpus trees can reach 7 meters in height with variable morphologies. Species of this genus are distributed from Nicaragua to northern Bolivia and southern Brazil, where they can be found mainly in the Atlantic Forest and the Amazon region. The main classes of secondary metabolites found in this genus are alkaloids and coumarins. The latter class is considered a chemical marker in the family, due to its abundant occurrence in Rutaceae.[3,7-8]

Alkaloids are an important class of secondary metabolites, containing one or more nitrogen atoms in their organic structure, found mainly in plants. Derived from an amino acid, alkaloids are classified according to the structure of their biosynthetic precursor, such as tropane, quinoline, isoquinoline, pyrrolidine, and indole, among others (Figure 1).[9-10]

In Rutaceae, the diversity of alkaloid production is considered atypical because its structural variety is in the alkaloids derived from anthranilic acid, mainly those of furan and pyranoquinoline types, as well as acridonic and quinazoline. Anthranilic acid is a key intermediate in the biosynthesis of L-tryptophan, but it can also function as an alkaloid precursor, using processes that retain the skeleton and exploit the carboxyl (Figure 2).[9,11-12]

Alkaloids have been widely studied due to their beneficial biological properties. Acridone alkaloids, for example, are used as antineoplastic agents against colon and lung carcinoma. The furoquinolines have anticholinesterase, antiviral, antiplasmodial, and antibacterial activities.

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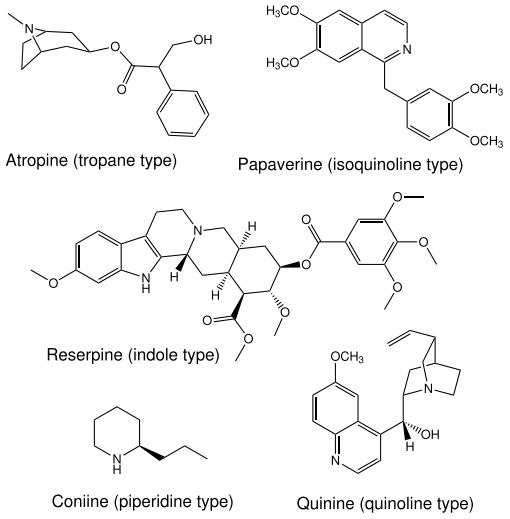


Figure 1. Some types of alkaloids

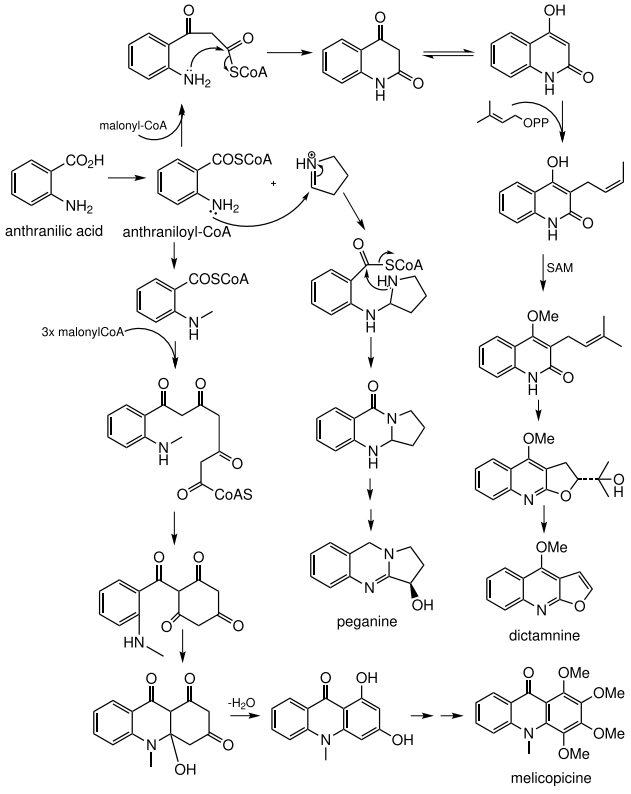


Figure 2. Anthranilic acid generating quinazoline, quinoline, and acridonic alkaloids

In addition, natural alkaloids also serve as a model for the chemical synthesis of analogues for testing biological properties.[13,14]

Another important secondary metabolite class found in Rutaceae, the coumarins, are heterocyclic structures containing a benzene ring fused to a pyran ring with a carbonyl in position 2 (Figure 3).[15]

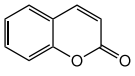


Figure 3. Basic structure of coumarin

Coumarin is biosynthesized primarily via the shikimic acid pathway, in which phosphoenolpyruvate (PEP) and D-erythrose 4-phosphate are condensed to form 3-D-arabinoheptulosonate 7-phosphate (DAHP), followed by elimination of phosphoric acid and an intramolecular aldol condensation, resulting in 3- dehydroquinic acid, which in turn is dehydrated and reduced by the enzyme NADPH (Figure 4).[9,15]

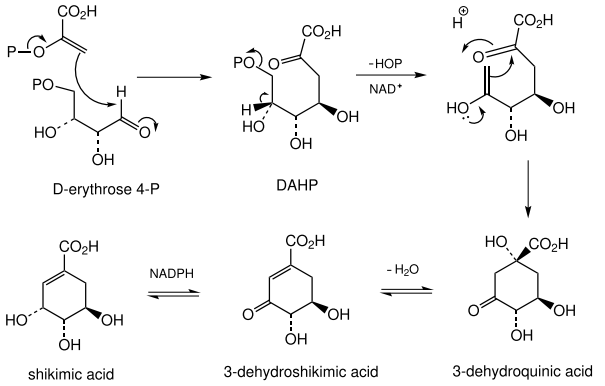


Figure 4. First stage of biosynthesis

The shikimic acid resulting from the first stage of biosynthesis, interacts with PEP, and after some intramolecular eliminations, gives rise to phenylalanine, which, by eliminating NH_2, generates cinnamic acid. Cinnamic acid is transformed into 2-coumaric acid and after isomerization and lactone formation, coumarin is formed (Figure 5).[9]

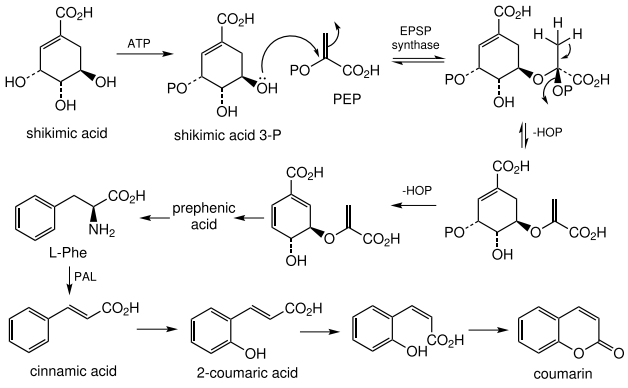


Figure 5. Second stage of biosynthesis

This class of secondary metabolites can be divided according to the different substitution positions, being classified into simple coumarins, furanocoumarins, pyranocoumarins, and coumarins substituted in the lactone ring. Simple coumarins are represented by basic coumarin (Figure 3) and its hydroxylated, methoxylated, or alkylated derivatives, with substitution at C-5, C-6, C-7, or C-8. Furanocoumarins have a furan ring attached to the coumarin nucleus, and can further be subdivided into linear and angular. Another group is called pyranocoumarins because they have a six-membered lactone ring attached to the

coumarin nucleus, and are also subdivided into linear and angular. Finally, there are coumarins that are substituted in the lactone ring, in the C-3 or C-4 position, which are rare to be found naturally.[16,17]

Considering the bioactivity of this class and its importance, we can check a wide range of pharmacotherapeutic applications, including anticoagulant, anticancer, anti-neurodegenerative, antioxidant, antiviral, antidiabetic, anti-inflammatory, antibacterial, antifungal, and antihypertensive activities.[15-17]

The medicinal use and constant presence of these two classes of secondary metabolites in Rutaceae, makes them stand out in the current work, since in the genus *Conchocarpus* this becomes relevant. Therefore, this work presents a review of the literature on alkaloids and coumarins, isolated from species of the genus *Conchocarpus*, describing the ^{1}H and ^{13}C NMR data of these secondary metabolites.

2. Experimental

The search for articles on the isolation of secondary metabolites was carried out using the digital platforms "periódicos CAPES", "Web of Science", "Scifinder" and "Google Scholar", until September 2023. The keywords used for this search were "*Conchocarpus* genus", "*Conchocarpus* phytochemistry"; "*Conchocarpus* alkaloids", "*Conchocarpus* coumarins", among others.

3. Results and Discussion

3.1. Alkaloids

Table 1 lists the alkaloids, the species from which they have been isolated, the respective plant origin, and the spectral data available for each; followed by their respective structures (Figure 6).

Conchocarpus alkaloids are divided into quinoline (**1-18**), acridonic (**19-37**), indolopyridoquinazoline (**38-50**), and piperidine (**51**), according to the types of alkaloids found in the family to which it belongs. The first group of alkaloids (**1-18**), can be further subdivided into furanoquinolines (**1-5**), pyranoquinolines (**11-14**), and quinolines with only a methyl or methoxyl substituent (**6-10**), or with an alkyl or phenyl substituent (**15-18**).

Tabela 1. Isolated alkaloids of the genus *Conchocarpus*

Compound	Species	Part	Data
Dictamnine (**1**)	*C. cyrtanthus*	Stem[18]	^{1}H-NMR, ^{13}C-NMR[22]
	C. fontanesianus	Stem[19]	
	C. inopinatus	Stem[20,21]	
γ-fagarine (**2**)	*C. fontanesianus*	Stem[19]	^{1}H-NMR[24], ^{13}C-NMR[25]
		Stem bark[23]	
	C. mastigophorus	Stem[57]	
Skimmianine (**3**)	*C. fontanesianus*	Stem[19]	^{1}H-NMR, ^{13}C-NMR[27]
		Stem bark[23]	
	C. longifolius	Stem[26]	
Confusameline (**4**)	*C. fontanesianus*	Stem bark[23]	^{1}H-NMR[28]
Haplopine (**5**)	*C. fontanesianus*	Stem bark[23]	^{1}H-NMR[29], ^{13}C-NMR[30]
Haplotusine (**6**)	*C. heterophyllus*	Stem[31]	^{1}H-NMR, ^{13}C-NMR[24]
	C. longifolius	Stem[26]	
	C. gaudichaudianus	Stem and twigs[32]	
	C. mastigophorus	Stem[57]	
4,6-dimethoxy-2-quinolone (**7**) N-methyl-4,6-dimethoxy-2-quinolone (**8**) 6-methoxy-haplotusine (**9**)	*C. longifolius*	Stem[26]	*
4-methoxy-1-methylquinolin-2(1H)-one (**10**)	*C. mastigophorus*	Stem[57]	^{1}H-NMR, ^{13}C-NMR[58]
Flindersine (**11**)	*C. fontanesianus*	Stem bark[23]	^{1}H-NMR, ^{13}C-NMR[33]
8-methoxyflindersine (**12**)	*C. fontanesianus*	Stem bark[23]	^{1}H-NMR, ^{13}C-NMR[34]
N-methyl-haplamine (**13**)	*C. longifolius*	Stem[26]	^{1}H-NMR, ^{13}C-NMR[35]
N-methoxy-haplamine (**14**)	*C. longifolius*	Stem[26]	*
4-methoxy-1-methyl-3-(3',7'-dimethyl-6',7'-dihydroxy-2'-octenyl)2-quinolone (**15**)	*C. gaudichaudianus*	Stem and leaves[32,36]	^{1}H-NMR, ^{13}C-NMR[36]
4-methoxy-1-methyl-3-(3',8'-dimethyl-7',8'-dihydroxy-2'-nonenyl)2-quinolone (**16**)	*C. gaudichaudianus*	Leaves[32]	*

Tabela 1. Isolated alkaloids of the genus *Conchocarpus* (cont.)

Compound	Species	Part	Data
2-phenyl-1-methyl-4-quinolone (**17**)	*C. fontanesianus*	Stem bark[23]	^{1}H-NMR, ^{13}C-NMR[24]
		Stem[19]	
	C. heterophyllus	Stem[31]	
	C. inopinatus	Stem[20,21]	
	C. marginatus	Stem[21,37]	
	C. mastigophorus	Stem[57]	
2-phenyl-1-methyl-7-methoxy-quinolin-4-one (**18**)	*C. marginatus*	Stem[21,37]	^{1}H-NMR, ^{13}C-NMR[37]
Arborinine (**19**)	*C. macrophyllus*	Stem[38,39]	^{1}H-NMR, ^{13}C-NMR[38]
	C. marginatus	Leaves[21,37,40]	
	C. inopinatus	Leaves[21,40]	
Methylarborinine (**20**)	*C. macrophyllus*	Stem[38]	^{1}H-NMR[38]
	C. inopinatus	Stem[20]	
	C. inopinatus	Leaves and stem[40]	
	C. marginatus	Leaves[37]	
		Leaves[21]	
	C. inopinatus	Stem[21]	
Xanthoxoline (**21**)	*C. inopinatus*	Leaves[21,40]	^{1}H-NMR, ^{13}C-NMR[41]
Toddaliopsin C (**22**)	*C. inopinatus*	Leaves[21]	^{1}H-NMR, ^{13}C-NMR[42]
1-hydroxy-3-methoxy-*N*-methyl acridone (**23**)	*C. marginatus*	Leaves[37]	^{1}H-NMR[41], ^{13}C-NMR[43]
	C. inopinatus	Leaves[21,40]	
1,2,3,5-tetramethoxy-*N*-methylacridone (**24**)	*C. inopinatus*	Leaves[21,40]	^{13}C-NMR[44]
1,2,3,6-tetramethoxy-10-methylacridone (**25**)	*C. marginatus*	Stem[37]	^{1}H-NMR, ^{13}C-NMR[37]
		Leaves[37]	
1-hydroxy-2,3,6-trimethoxy-*N*-methylacridone (**26**)	*C. marginatus*	Stem[37]	^{1}H-NMR, ^{13}C-NMR[37]
1-hydroxy-2,3,6-trimethoxy-acridone (**27**)	*C. marginatus*	Stem[37]	^{1}H-NMR, ^{13}C-NMR[37]
1-hydroxy-3,6-dimethoxy-N-methylacridone (**28**)	*C. marginatus*	Leaves[37]	^{1}H-NMR, ^{13}C-NMR[37]
Cuspanine (**29**)	*C. paniculatus*	Leaves[45]	^{1}H-NMR, ^{13}C-NMR[45]
1-hydroxy-2,3-dimethoxy-*N*-methyleneacethoxyacridone (**30**)	*C. inopinatus*	Leaves[40]	*
Cusculine (**31**)	*C. paniculatus*	Leaves[45]	^{1}H-NMR, ^{13}C-NMR[45]
1,3,6-trihydroxy-2,4,5-trimethoxy-10-methylacridin-9(10*H*)-one (**32**)	*C. mastigophorus*	Stem[57]	^{1}H-NMR, ^{13}C-NMR[57]
Citramine (**33**)	*C. mastigophorus*	Stem[57]	^{1}H-NMR, ^{13}C-NMR[59]
Citrusinine I (**34**)			^{1}H-NMR[60]
Glyfoline (**35**)			^{1}H-NMR[61]
Citbrasine (**36**)			^{1}H-NMR[62]
Inopinatin (**37**)	*C. inopinatus*	Leaves[21,40]	^{1}H-NMR, ^{13}C-NMR[21]
3-(2-(7,7-dimethyl-3,7-dihydropyran[3,2-e]indol-1- yl)etyl)quinazoline-2,4(1H,3H)-dione (**38**)	*C. gaudichaudianus*	Stem[36] / Stem and twigs[32]	^{1}H-NMR, ^{13}C-NMR[36]
3-(2-(7,7-dimethyl-3,7-dihydropyran- [3,2-e]indol-1-yl)etyl)-1-hydroxyquinazoline-2,4(1H,3H)-dione (**39**)	*C. gaudichaudianus*	Stem[36] / Twigs[32]	^{1}H-NMR, ^{13}C-NMR[36]
3-(2-(7,7- dimethyl-3,7-dihydropyran[3,2-e]indol-1-yl)etyl-1-methylquinazoline-2,4(1H,3H)-dione (**40**)	*C. gaudichaudianus*	Stem[36]	^{1}H-NMR, ^{13}C-NMR[36]
	C. macrocarpus	Stem[39]	
	C. gaudichaudianus	Stem and twigs[32]	
Hydroxy-indolquinazoline (**41**)	*C. macrocarpus*	Stem[39]	*
9,10-(2,2-dimethylcromene)3-hydroxy-14-dimethylgoshyyuamide II (**42**)	*C. gaudichaudianus*	Stem[32]	
9,10-(2-methoxycromene)3-hydroxy-14-dimethylgoshyyuamide II (**43**)			
10-hydroxyrutaecarpine (**44**)	*C. fontanesianus*	Stem bark[23]	^{1}H-NMR, ^{13}C-NMR[46]
10,18-dihydroxyrutaecarpine (**45**)	*C. fontanesianus*	Stem bark[23]	^{1}H-NMR, ^{13}C-NMR[23]

Tabela 1. Isolated alkaloids of the genus *Conchocarpus* (cont.)

Compound	Species	Part	Data
Conchacarpine B (**46**)			
Fontanesine A (**47**)			
Fontanesine B (**48**)	*C. fontanesianus*	Stem bark[23]	^{1}H-NMR, ^{13}C-NMR[23]
Fontanesine C (**49**)			
Conchacarpine A (**50**)			
(3S)-(-)-3-hydroxy-1-methylpiperidin-2-one (**51**)	*C. mastigophorus*	Stem[57]	^{1}H-NMR, ^{13}C-NMR[57]

*Data not found

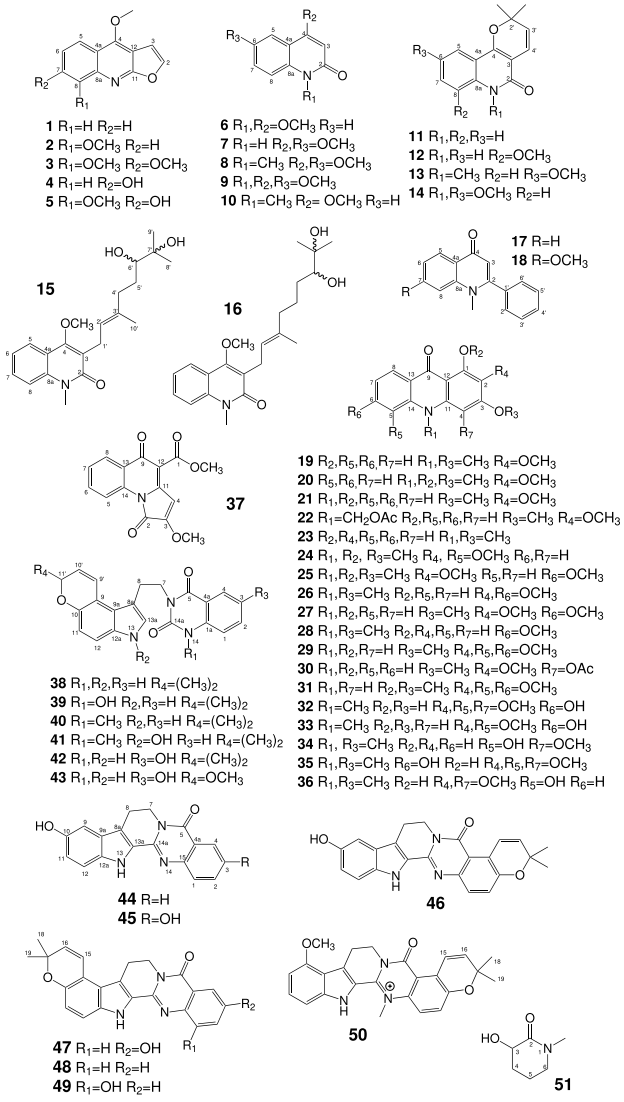


Figure 6. Alkaloids from *Conchocarpus* species

Tables 2 and 3 show the ^{1}H and ^{13}C-NMR data of the isolated compounds.

Furanoquinoline alkaloids (**1-5**) show two doublets with the same coupling constant in the ^{1}H NMR spectrum, demonstrating the interaction between hydrogens H-2 and H-3, with chemical shift values of approximately δ_H 7.70 for H- 2 and δ_H 7.10 for H-3. In addition, another doublet with coupling between them can be noticed for the hydrogens H-5 and H-6, with increased values in relation to H-2 and H-3. Values referring to H-7 and H-8 appear when they are not replaced between δ_H 7.00-8.00, and methoxyl hydrogens appear as a singlet around δ_H 4.00. The different *J* values in H-8 for compounds **1** and **4** are due to the fact that in **1** the *J* value at 8.5 Hz refers to *ortho*-coupling, while in **4** this value is lower due to meta-coupling between H-8 and H-6.

Pyranoquinoline alkaloids (**11-14**) show H-5 to H-8 values between δ_H 7.00-8.00, as expected for aromatic hydrogens, with some lower values being seen when they are in the *ortho* to methoxyl position. The hydrogens H-3' and H-4' have values of δ_H 5.50 and δ_H 6.70, respectively, due to the γ effect of carbonyl protection, lowering the value of H-3, and the β effect of deprotection of carbonyl, increasing the value of H-4. The pyran ring of this group of alkaloids is in positions 3 and 4, and not in positions 2 and 3, because if it were in 2 and 3 there should be two more hydrogen signs, which refer to H-2 and H-4.

Compounds **15** and **16** contain a prenylated group and this can be confirmed due to the chemical shifts of hydrogens H-1' until H-10', which are hydrogens with much lower values, corresponding to hydrogens -CH3, -CH2 and -CH of open-chain saturated carbons. The presence of some unsaturations in the prenyl group results in higher values, such as 5.30 in H-2'. This shows the difference between prenylated alkaloids (**15-16**) and pyranoquinoline alkaloids (**11-14**) that have chemical shifts related to aromatic hydrogens.

Acridonic alkaloids (**19-36**) also have a carbonyl effect on H-8, with values above δ_H 8.00, showing deprotection in the β carbonyl position, unlike hydrogen H-7, which is in the γ position of carbonyl protection, presenting values below δ_H 7.50. Another effect already mentioned is the methoxyl electron donor seen in hydrogen H-5 in the *ortho* position; when there is substitution of the –OCH_3 group on carbon 6, the value of H-5 is close to δ_H 6.70, and when there is no substitution on carbon 6 this value is around δ_H 7.50. The same reduction in values occurs with hydrogen H-4, since there is substitution on carbon 3 by methoxyl.

The piperidine alkaloid **51** has ^{1}H signs consistent with its substituents, since H-3 has a high value due to the hydroxyl linked to it. Hydrogen H-6 also has a value above δ_H 3.10 because it has nitrogen as a neighbor, increasing the value of methylene hydrogen.

The last type of alkaloid isolated from *Conchocarpus*, has an indole part and a quinazoline part in its skeleton,

Table 2. ^{1}H-NMR data (in $CDCl_3$) of alkaloids from *Conchocarpus* species. (Multiplicities, *J*, in parenthesis)

H	Compound/δ_H (ppm), J_H (Hz)						
	1*	**2**	**3**	**4****	**5**	**6**	**10**
2	7.71 (*d*, 2.0)	7.65 (*d*, 2,8)	7.55 (*d,* 3.0)	7.90 (*d*, 2.8)	7.55 (*d*, 3.0)		
3	7.21 (*d*, 2.0)	7.09 (*d*, 2,8)	7.00 (*d,* 3.0)	7.37 (*d*, 2.8)	7.03 (*d*, 3.0)	6.08 (*s*)	6.06 (*s*)
5	8.09 (*d,* 8.5)	7.85 (*dd*, 8.4; 1.2)	7.98 (*d,* 9.4)	8.06 (*d*, 9.0)	7.14 (*d*, 9.0)	8.00 (*dl*, 8.0)	7.35 (*dd*, 5.7; 0.6)
6	7.38 (*t*, 8.5)	7.37 (*t*, 8.4)	7.21 (*d,* 9.4)	7.03 (*dd*, 2.4; 9.0)	7.94 (*d*, 9.0)	7.34 (*ddd*, 8.0; 6.4; 1.6)	7.60 (*ddd*, 5.7; 4.8; 1.0)
7	7.65 (*t*, 8.5)	7.07 (*dd*, 8.4; 1.2)					7.24 (*ddd*, 5.3; 4.8; 0.6)
8	7.78 (*d*, 8.5)			7.11 (*d*, 2.4)			7.99 (*dd*, 5.3; 1.0)
4-OCH_3	4.37 (*s*)	4.46 (*s*)	4.40 (*s*)	4.40 (*s*)	4.42 (*s*)		3.97 (*s*)
7-OCH_3			4.02 (*s*)				
8-OCH_3		4.09 (*s*)	4.12 (*s*)		4.19 (*s*)		
OH				10.04 (*s*)			
***N*-CH_3**							3.70 (*s*) **H**

H	Compound/δ_H (ppm), J_H (Hz)						
	11	**12**	**13**	**15**	**17**	**18**	**19**
3					6.67 (*s*)	6.26 (*s*)	
4							6.29 (*s*)
5	7.88 (*d*, 8.4)	7.44 (*dd*, 8.1; 0.9)	7.37 (*d*, 2.8)	7.84 (*dd*, 7.8; 1.5)	8.51 (*dd*, 8.1 e 1.4)	8.43 (*d*, 9.2)	7.46 (*dl,* 8.6)
6	7.18 (*t*, 6.8)	7.09 (*t*, 8.1)		7.27 (*td*, 7.8; 0.9)	7.52 (*m*)	7.03 (*dd*, 9.2; 2.8)	7.68 (*ddd*, 8.6; 7.0; 1.6)
7		6.92 (*dd*, 8.1; 0.9)	7.18 (*dd*, 9.0; 2.8)	7.55 (*td*, 7.8; 1.5)	7.81 (*ddd*, 8.5; 7.0; 1.4)		7.25 (*ddd*, 8.0; 7.0; 0.8)
8			7.26 (*d*, 9.0)	7.38 (*dd*, 7.8; 0.9)	7.67 (*dl*, 8.5)	6.88 (*d*, 2.8)	8.42 (*dd*, 8.0; 1.6)
1'				3.37 (*d*, 6.6)			
2'				5.30 (*td*, 6.6; 1.1)	7.44 (*m*)	7.42 (*m*)	
3'		5.51 (*d*, 10.2)	5.55 (*d*, 11.0)		7.53 (*m*)	7.52 (*m*)	
4'		6.70 (*d*, 9.9)	6.76 (*d*, 11.0)	1.96-2.07 (*m*); 2.20-2.29 (*m*)	7.53 (*m*)	7.52 (*m*)	
5'				1.72-1.62 (*m*); 1.42-1.26 (*m*)	7.53 (*m*)	7.52 (*m*)	
6'				3.22 (*dd*, 10.4; 1.6)	7.44 (*m*)	7.42 (*m*)	
8'				1.07 (*s*)			
9'				1.07 (*s*)			
10'				1.80 (*sl*)			
2'-CH_3		1.51 (*s*)	1.52 (*s*)				
2-OCH_3							3.87 (*s*)
3-OCH_3							3.97 (*s*)
-OCH_3		3.94 (*s*)	3.90 (*s*)	3.94 (*s*)		3.95 (*s*)	
***N*-CH_3**			3.68 (*s*)	3.69 (*s*)	3.74 (*s*)	3.56 (*s*)	3.80 (*s*)
NH		9.11 (*s*)					
OH							14.72 (*s*)

H	Compound/δ_H (ppm), J_H (Hz)						
	20	**21***	**22**	**23**	**25**	**26**	**27**
2				7.31 (*d*, 1.5)			
4	6.29 (*s*)	6.50 (*s*)	6.59 (*s*)	6.21 (*d*, 1.5)	6.49 (*s*)	6.14 (*s*)	6.18 (*s*)

Table 2. ^{1}H-NMR data (in $CDCl_3$) of alkaloids from *Conchocarpus* species. (Multiplicities, *J*, in parenthesis) (cont.)

H	Compound/δ_H (ppm), J_H (Hz)						
	20	**21***	**22**	**23**	**25**	**26**	**27**
5	7.55 (*dl*, 8.6)	7.51 (*dl*, 8.2)	7.58 (*d*, 8.6)	7.42 (*dl*, 8.6)	6.64 (*d*, 2.4)	6.71 (*d*, 2.0)	6.61 (*d*, 2.4)
6	7.76 (*ddd*, 8.6; 7.0; 1.6)	7.70 (*ddd*, 8.2; 7.5; 1.4)	7.73 (*dd*, 8.6; 7.1)	7.69 (*ddd*, 8.6; 7.6; 0.8)			
7	7.35 (*ddd*, 8.0; 7.0; 0.8)	7.29 (*ddl*, 8.0; 7.5)	7.34 (*dd*, 8.1; 7.1)	7.25 (*tl*, 7.6)	6.80 (*dd*, 9.2; 2.4)	6.80 (*dd*, 8.8; 2.0)	6.85 (*dd*, 9.2; 2.4)
8	8.51 (*dd*, 8.0; 1.6)	8.26 (*dd*, 8.2; 1.4)	8.41 (*d*, 8.1)	8.38 (*dd*, 8.0; 0.8)	8.39 (*d*, 9.2)	8.25 (*d*, 8.8)	8.24 (*d*, 9.2)
1-OCH_3	4.05 (*s*)				4.02 (*s*)		
2-OCH_3	3.95 (*s*)	3.75 (*s*)	3.90 (*s*)		3.91 (*s*)	3.91 (*s*)	3.92 (*s*)
3-OCH_3	3.89 (*s*)	3.90 (*s*)	3.99 (*s*)	3.88 (*s*)	3.98 (*s*)	3.98 (*s*)	3.93 (*s*)
6-OCH_3					3.89 (*s*)	3.94 (*s*)	3.90 (*s*)
***N*-CH_3**	3.50 (*s*)			3.72 (*s*)	3.65 (*s*)	3.68 (*s*)	
***N*-CH_2**			6.33 (*sl*)				
NH		10.93 (*sl*)					
OH		14.22 (*s*)		14.82 (*s*)			14.15 (*s*)
CH_3(Ac)			2.19 (*s*)				

H	Compound/δ_H (ppm), J_H (Hz)					
	28	**29**	**31**	**32**	**33*** **	**34***
1						
2	6.27 (*d*, 2.0)					6.39 (*s*)
3						
4	6.25 (*d*, 2.0)	6.23 (*s*)	6.48 (*s*)		6.48 (*s*)	
5	6.77 (*d*, 2.0)					
6						7.13-7.21 (*m*)
7	6.85 (*dd*, 9.2; 2.0)	6.92 (*d*, 8.0)	6.86 (*d*, 8.0)	6.95 (*d*, 8.8)	6.95 (*d*, 9.1)	7.13-7.21 (*m*)
8	8.34 (*d*, 9.2)	8.06 (*d*, 8.0)	8.10 (*d*, 8.0)	7.94 (*d*, 8.8)	8.05 (*d*, 9.1)	7.76 (*dl*, 6.9)
2-OCH_3				3.87 (*s*)	3.87 (*s*)	
3-OCH_3	3.95 (*s*)					3.85 (*s*)
4-OCH_3				3.83 (*s*)		3.97 (*s*)
5-OCH_3				3.86 (*s*)	3.78 (*s*)	
6-OCH_3	3.89 (*s*)					
***N*-CH_3**	3.70 (*s*)			3.75 (*s*)	4.04 (*s*)	3.79 (*s*)
NH		8.44 (*sl*)	8.30 (*sl*)			
1-OH				14.38 (*s*)		
3-OH				8.90 (*s*)	8.96 (*s*)	
5-OH						9.88 (*sl*)
6-OH				9.11 (*s*)	8.96 (*s*)	
-OCH_3		4.02 (*s*); 4.00 (*s*); 3.95 (*s*); 3.90 (*s*)	4.00 (*s*); 3.98 (*s*); 3.95 (*s*); 3.92 (*s*); 3.88 (*s*)			

H	Compound/δ_H (ppm), J_H (Hz)					
	35**	**36**	**37**	**38****	**39****	**40****
1				7.19 (*d*, 8.1)	7.22 (*d*, 8.1)	7.45 (*d*, 8.1)
2				7.65 (*td*, 8.1; 1.3)	7.66 (*t*, 8.1)	7.78 (*td*, 8.1; 1.8)
3				7.21 (*t*, 8.1)	7.22 (*t*, 8.1)	7.31 (*t*, 8.1)
4			6.70 (*s*)	7.95 (*dd*, 8.1; 1.3)	7.96 (*d*, 8.1)	8.05 (*dd*, 8.1; 1.5)

Table 2. [1]H-NMR data (in $CDCl_3$) of alkaloids from *Conchocarpus* species. (Multiplicities, *J*, in parenthesis) (cont.)

H	Compound/δ_H (ppm), J_H (Hz)							
	35**	**36**	**37**	**38****	**39****	**40****		
5			8.77 (*dd*, 8.5; 0.5)					
6		7.19 (*dd*, 2.0; 8.0)	7.66 (*ddd*, 8.5; 7.2; 1.5)					
7	6.94 (*d*, 9.0)	7.07 (*t*, 8.0)	7.37 (*ddd*, 8.0; 7.2; 1.0)	4.13 (*t*, 8.1)	4.14 (*t*, 8.1)	4.18 (*t*, 7.8)		
8	7.84 (*d*, 9.0)	7.85 (*dd*, 2.0; 8.0)	8.23 (*dd*, 8.0; 1.5)	3.02 (*t*, 8.1)	3.02 (*t*, 8.1)	3.02 (*t*, 7.8)		
11				6.56 (*d*, 8.7)	6.57 (*d*, 8.5)	6.56 (*d*, 8.7)		
12				7.08 (*d*, 8.7)	7.09 (*d*, 8.5)	7.08 (*d*, 8.7)		
13a				7.13 (*s*)	7.15 (*d*, 2.4)	7.15 (*d*, 2.4)		
9'				7.28 (*d*, 9.8)	7.28 (*d*, 9.8)	7.26 (*d*, 9.6)		
10'				5.72 (*d*, 9.8)	5.69 (*d*, 9.8)	5.69 (*d*, 9.6)		
12'				1.35 (*s*)	1.35 (*s*)	1.34 (*s*)		
13'				1.35 (*s*)	1.35 (*s*)	1.34 (*s*)		
1-OCH_3			3.98 (*s*)					
2-OCH_3		4.13 (*s*)						
3-OCH_3		3.95 (*s*)	4.03 (*s*)					
4-OCH_3		3.81 (*s*)						
6-OCH_3								
***N*-CH_3**	4.02 (*s*)	3.84 (*s*)				3.55 (*s*)		
13-NH				10.44 (*s*)	11.53 (*s*)	10.76 (*d*, 2.4)		
14-NH				11.43 (*s*)				
OH					10.80 (*d*, 2.4)			
1-OH	14.18 (*s*)	13.99 (*s*)						
5-OH		7.12 (*s*)						
6-OH	10.45 (*s*)							
-OCH_3	3.69 (*s*); 3.75 (*s*); 3.78 (*s*); 3.80 (*s*)							

H	Compound/δ_H (ppm), J_H (Hz)							
	44**	**45***	**46***	**47****	**48****	**49****	**50***	**51***
1	7.66 (*dl*, 8.7)	7.59 (*d*, 8.7)	7.45 (*d*, 8.7)	7.56 (*d*, 8.8)	7.67 (*dd*, 8.3; 1.2)		7.78 (*d*, 9.2)	
2	7,80 (*ddd*, 1.5; 7.2; 8.7)	7.28 (*dd*, 8.7; 2.8)	7.17 (*d*, 8.7)	7.28 (*dd*, 8.8; 2.9)	7.81 (*ddd*, 8.3; 7.1; 1.5)	7.20 (*dd*, 7.9; 1.3)	7.44 (*d*, 9.2)	
3	7.47 (*ddd*, 1.5; 7.2; 7.8)				7.47 (*ddd*, 8.0; 7.1; 1.2)	7.29 (*t*, 7.9)		3.81 (*dd*, 9.3; 6.9)
4	8.15 (*dl*, 7.8)	7.54 (*d*, 2.8)		7.48 (*d*, 2.9)	8.16 (*dd*, 8.0; 1.5)	7.55 (*dd*, 7.9; 1.3)		2.13 (*m*); 2.48 (*m*)
5								1.99 (*m*); 2.10 (*m*)
6								3.13 (*ddd*, 7.5; 9.1; 11.4); 3.75 (*ddd*, 4.0; 7.6; 11.5)
7	4.43 (*dd*, 6.3; 7.5)	4.52 (*t*, 6.8)	4.43 (*t*, 6.9)	4.41 (*t*, 6.8)	4.43 (*t*, 6.9)	4.41 (*t*, 6.9)	4.51 (*t*, 6.9)	
8	3.15 (*dd*, 6.3; 7.5)	3.14 (*t*, 6.8)	3.10 (*t*, 6.9)	3.29 (*t*, 6.8)	3.33 (*t*, 6.9)	3.35 (*t*, 6.9)	3.51 (*t*, 6.9)	
9	7.30 (*d*, 2.4)	6.95 (*d*, 2.3)	6.91 (*d*, 2.3)					
10							6.64 (*d*, 7.8)	

Table 2. ^{1}H-NMR data (in $CDCl_3$) of alkaloids from *Conchocarpus* species. (Multiplicities, *J*, in parenthesis) (cont.)

H	Compound/δ_H (ppm), J_H (Hz)							
	44**	**45***	**46***	**47****	**48****	**49****	**50***	**51***
11	7.04 (*dd*, 9.0; 2.4)	6.85 (*dd*, 8.8; 2.3)	6.83 (*dd*, 8.8; 2.3)	6.74 (*d*, 8.7)	6.77 (*d*, 8.7)	6.79 (*d*, 8.7)	7.42 (*t*, 8.5; 7.8)	
12	7.37 (*d*, 9.0)	7.31 (*d*, 8.8)	7.27 (*d*, 8.8)	7.23 (*d*, 8.7)	7.25 (*d*, 8.7)	7.29 (*d*, 8.7)	7.18 (*d*, 8.5)	
15			7.96 (*d*, 10.2)	6.86 (*d*, 9.7)	6.88 (*d*, 9.8)	6.88 (*d*, 9.8)	7.94 (*d*, 10.3)	
16			5.80 (*d*, 10.2)	5.74 (*d*, 9.7)	5.77 (*d*, 9.8)	5.78 (*d*, 9.8)	6.05 (*d*, 10.3)	
18,19-CH_3			1.44 (*s*)	1.38 (*s*)	1.40 (*s*)	1.40 (*s*)	1.49 (*s*)	
9-OCH_3							3.99 (*s*)	
14-*N*-CH_3							4.32 (*s*)	
13-NH	11.76 (*sl*)				11.72 (*s*)	11.40 (*s*)		
10-OH	8.31 (*sl*)							
16-OH						9.23 (*s*)		
***N*-CH_3**								2.94 (*s*)

* Spectrum recorded in CD_3OD; ** Spectrum recorded in DMSO; *** Spectrum recorded in C_3D_6O

Table 3. ^{13}C-NMR data (in $CDCl_3$) of alkaloids from *Conchocarpus* species

C	Compound/δ_C (ppm)						
	1*	**2**	**3**	**5****	**6**	**10**	**11**
2	143.6	143.9	143.0	142.1		163.8	163.1
3	104.2	104.5	104.7	105.5	96.9	96.5	105.9
4	157.0	156.8	157.2	156.9	164.6	162.6	157.4
4a	102.5	103.8	114.9	101.2	116.9	116.5	115.4
5	121.8	114.0	118.2	117.9	124.5	131.2	122.6
6	123.7	123.4	112.0	116.5	124.2	121.6	122.2
7	129.8	107.6	152.1	141.4	133.3	123.3	130.9
8	128.0	154.5	142.0	139.3	113.1	114.0	116.4
8a	145.1	137.4	141.5	150.2	138.1	139.7	138.3
11	162.6	163.2	164.4	163.8			
12	117.0	119.6	102.0	113.3			
2'							79.2
3'							126.3
4'							117.4
4-OCH_3	58.0	59.0	59.0	59.2		55.8	
7-OCH_3			56.8				
8-OCH_3		55.9	61.7	60.8			
2'-CH_3							28.5
***N*- CH_3**						29.0	

C	Compound/δ_C (ppm)							
	12	**13**	**15**	**17**	**18**	**19**	**21***	**22**
1						156.2	155.7	156.1
2	160.6	160.1	164.2	156.9	154.5	129.9	130.4	131.0
3	106.2	105.9	123.7	111.1	112.5	159.3	160.6	159.6
4	157.0	154.2	161.2	174.5	176.8	86.7	88.4	87.5
4a	115.6	116.3	118.5	126.4	120.9			
5	114.4	104.3	124.2	126.4	128.5	114.5	117.3	114.6
6	121.6	154.2	122.8	125.3	112.5	133.9	134.2	134.4
7	110.2	119.2	131.3	133.7	163.1	121.4	122.0	122.7
8	145.4	115.1	115.4	116.6	99.3	126.7	126.0	126.7

Table 3. ^{13}C-NMR data (in $CDCl_3$) of alkaloids from *Conchocarpus* species (cont.)

C	Compound/δ_C (ppm)							
	12	**13**	**15**	**17**	**18**	**19**	**21***	**22**
8a	127.9	133.6	140.4	141.5	143.5			
9						180.9	181.8	181.6
10						140.6	140.2	139.7
11						105.3	106.4	105.5
12						120.8	113.1	121.0
13						142.0	141.5	141.7
1'			24.7	134.7	135.6			
2'	79.0	78.5	122.7	128.6	128.6			
3'	126.1	126.1	136.7	129.1	129.0			
4'	117.1	117.8	37.7	130.3	129.4			
5'			30.1	129.1	129.0			
6'			78.5	128.6	128.5			
7'			72.8					
8'			25.8					
9'			25.2					
10'			16.5					
2-OCH_3						60.8	60.2	60.8
3-OCH_3						56.0	56.1	56.2
4-OCH_3			30.4					
6-OCH_3		55.5						
7-OCH_3					55.0			
8-OCH_3	55.9							
2'-CH_3	28.2	28.0						
***N*-CH_3**		29.1	62.3	38.4	37.4	34.1		
***N*-CH_2**								70.3
CH_3 (Ac)							20.9	
C=O (Ac)							170.4	

C	Compound/δ_C (ppm)						
	23	**24**	**25**	**26**	**27**	**28**	**29**
1	164.6	153.9	154.6	156.4		164.4	155.5
2	94.3	138.0	137.9	130.4	130.2	90.3	130.3
3	165.7	157.9	157.4	158.9	159.2	165.6	159.4
4	89.7	93.9	93.0	86.9	87.3	94.1	87.6
5	115.7	149.7	97.9	97.9	101.3	97.9	135.0
6	134.2	114.8	163.5	164.4	164.2	164.4	154.5
7	121.3	122.1	109.3	110.0	111.8	110.1	107.6
8	125.4	119.0	129.6	128.3	128.1	128.9	122.1
9	179.6	176.9	175.7	180.2	180.6	179.9	181.14
11	144.4	145.0	141.9	140.6	138.1	144.9	138.1
12	104.3	112.7	112.0	105.5	104.8	104.7	104.5
13	119.9	127.4	118.4	115.3	113.7	115.9	114.7
14	141.9	135.0	143.6	144.0	141.9	144.0	133.7
1-OCH_3		61.9	61.8				
2-OCH_3		61.6	61.4	60.8	60.9		
3-OCH_3	55.5	56.1	55.9	55.7	56.2	55.5	
5-OCH_3		56.5					
6-OCH_3			55.5	56.1	56.2	55.5	

Table 3. ^{13}C-NMR data (in $CDCl_3$) of alkaloids from *Conchocarpus* species (cont.)

C	Compound/δ_C (ppm)						
	23	**24**	**25**	**26**	**27**	**28**	**29**
***N*-CH$_3$**	34.0	42.4	34.6	34.2		34.4	
-OCH$_3$							61.05; 60.88; 56.23; 56.08

C	Compound/δ_C (ppm)						
	31	**32**	**33****	**37**	**38****	**39****	**40****
1	154.6	152.7	156.0	164.8	115.6	115.2	114.7
1a					139.9	139.4	140.6
2	133.6	130.8	129.7	162.0	135.5	134.9	135.4
3	158.0	152.4	158.1	154.3	122.9	122.4	122.9
4	93.8	130.0	92.4	101.8	127.9	127.4	127.9
4a					114.3	114.2	114.7
5	134.3	137.2	136.0	116.4	162.6	161.9	161.3
6	153.9	156.9	157.0	134.7			
7	107.0	113.4	113.1	125.6	41.7	41.5	42.6
8	123.0	123.2	123.2	127.3	25.4	25.3	25.2
8a					111.2	110.6	110.9
9	176.2	182.6	180.8	176.0	112.5	112.5	112.0
9a					122.9	122.4	122.9
10					146.2	145.5	145.9
11	138.1	139.0	143.9	113.0	112.1	111.6	111.0
12	110.4	105.4	104.8	149.9	112.5	111.6	111.7
12a					132.9	132.3	132.5
13	117.4	118.0	116.7	123.7			
13a					125.4	124.8	125.0
14	139.4	143.3	139.6	136.2			
14a					150.7	150.1	150.6
9'					120.6	120.2	120.3
10'					129.9	129.3	129.5
11'					74.7	74.1	74.4
12'					27.2	27.1	27.1
13'					27.5	27.1	27.1
1-OCH$_3$				52.8			
2-OCH$_3$		60.6	60.4				
4-OCH$_3$		61.0					
5-OCH$_3$		60.8	61.3				
7-OCH$_3$				59.0			
***N*-CH$_3$**		46.3	40.1				
14-*N*-CH$_3$							30.8
- OCH$_3$	61.9; 61.5; 60.9; 56.1; 56.0						

C	Compound/δ_C (ppm)							
	44**	45*	46*	47**	48**	49**	50*	51*
1	126.9	129.2	128.7	128.1	126.4	151.8	119.4	
1a	147.9	142.4	144.7	140.5	147.4	135.8	136.3	
2	134.9	125.0	125.3	123.8	134.3	116.5	126.0	173.2
3	126.4	157.1	152.8	155.7	125.9	112.1	154.4	72.0
4	127.0	110.6	120.8	109.6	126.5	115.9	122.4	30.1

Table 3. [13]C-NMR data (in $CDCl_3$) of alkaloids from *Conchocarpus* species (cont.)

C	Compound/δ_C (ppm)							
	44**	45*	46*	47**	48**	49**	50*	51*
4a	121.1	122.7	116.6	121.6	120.6	120.8	115.1	
5	161.1		163.4	160.2	160.5	160.0		24.0
6								57.2
7	41.3	42.4	42.3	40.6	40.6	40.2	43.0	41.4
8	19.4	20.2	20.5	20.8	20.7	20.5	21.6	
8a	117.6	117.4	117.8	115.3	116.5	115.3	132.2	
9a	125.5	127.1	127.3	121.0	120.9	121.0	116.7	
9	106.2	103.8	104.0	112.5	112.6	112.5	157.4	
10	152.4	152.2	152.3	146.1	146.2	145.9	101.4	
11	118.0	116.5	116.7	115.0	115.6	115.2	131.6	
12	113.5	113.5	113.7	112.6	112.7	126.2	106.8	
12a	135.3	135.0	135.3	134.2	134.4	133.8	144.8	
13a	128.2	128.6	128.4	128.2	127.9	128.1	119.8	
14a	145.7	144.1	144.8	142.5	145.2	143.1	149.3	
15			122.1	119.2	119.2	118.8	120.4	
16			132.6	130.0	130.1	129.9	135.7	
17			76.7	75.0	75.0	74.8	77.6	
14-*N*-CH_3							41.5	
9-OCH_3							55.8	
18,19-CH_3			27.7	27.0	27.0	26.6	27.7	

* Spectrum recorded in CD_3OD; ** Spectrum recorded in DMSO

linked by a pyridine nucleus, or seco-pyridine, and for this reason, these alkaloids are called indolopyridoquinazolines (**38-50**). The hydrogens H-1, H-2, and H-3 of these alkaloids have values that are consistent with hydrogens in the aromatic region. Hydrogen H-4 has a higher value, due to carbonyl deprotection at the β position. The hydrogens H-7 and H-8 are methylene hydrogens, with increased values because they are close to an electronegative atom.

The [13]C NMR signals follow the chemical shift values corresponding to the substituent groups. When replaced by oxygen or nitrogen, that is, electronegative groups, there is an increase in the deshielding effect, increasing the chemical shift value of these carbons. Just like when there are sp^2 carbons, where the higher the "*s*" character, the more electronegative the carbon is, making the chemical shift value increase.

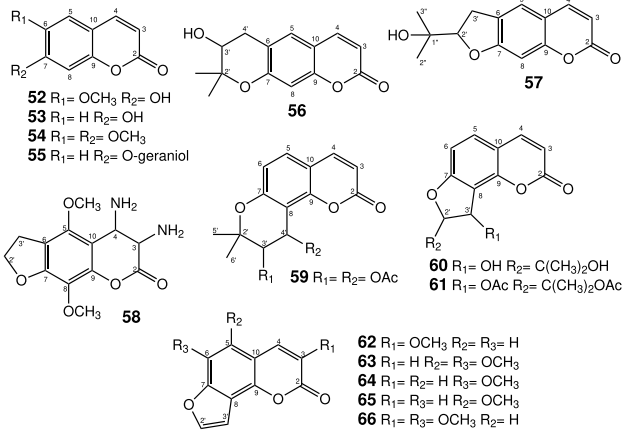


Figure 7. Coumarins from *Conchocarpus* species

3.2. Coumarins

Table 4 lists the coumarins, the species from which they have been isolated, the respective plant origin, and the spectral data available for each; followed by their respective structures (Figure 7).

Tables 5 and 6 show the [1]H and [13]C-NMR data of the isolated compounds.

The identification of coumarins is performed by understanding some specific signals of this class of secondary metabolites in the [1]H NMR spectrum. The unsubstituted coumarins on the lactone ring have characteristic signals on the H-3 and H-4 hydrogens, represented by two doublets with a coupling constant (*J*) between 9 and 10 Hz, and with a chemical shift around δ_H 6.30 corresponding to the H-3 and δ_H 7.60 corresponding to H-4. This occurs due to the presence of the double bond between the carbons of these hydrogens, together with the anisotropic effect of the aromatic ring and the mesomeric effect received by the conjugation of the carbonyl.

In the current review, it was identified that the genus *Conchocarpus* comprises four isolated coumarins of the simple type. In simple coumarins (**52-55**), a doublet is

Table 4. Isolated coumarins of the genus *Conchocarpus*

Compound	Species	Part	Data
Scopoletin (52)	*C. inopinatus*	Stem [20,21]	^{1}H-NMR [20], ^{13}C-NMR [50]
		Leaves [21]	
	C. longifolius	Petiole [26]	
Umbellioferone (53)	*C. longifolius*	Petiole [26]	^{1}H-NMR, ^{13}C-NMR [51]
Scoparone (54)	*C. longifolius*	Stem [26]	^{1}H-NMR, ^{13}C-NMR [52]
	C. inopinatus	Leaves [40]	
Auraptene (55)	*C. longifolius*	Leaves [40]	^{1}H-NMR, ^{13}C-NMR [53]
Aegelinol (56)	*C. fontanesianus*	Stem bark [23]	^{1}H-NMR, ^{13}C-NMR [8]
Marmesin (57)	*C. inopinatus*	Stem [20,21]	^{1}H-NMR, ^{13}C-NMR [54]
	C. mastigophorus	Stem [57]	
5,6-diamino-4,9-dimethoxy-2,3,5,6-tetrahydro-7H-furo[3,2g]chromen-7-one (58)	*C. longifolius*	Petiole [26]	*
Kellactone diacetato (59)	*C. longifolius*	Petiole and leaves [40,19]	^{13}C-NMR [55]
		Stem [48]	
3'-hydroxycolumbianetin (60)	*C. longifolius*	Stem [26]	*
Acetate de 8-[1-(acetyloxy)1-methylenil]2-oxo-8,9-dihydro-2H-furo-[2,3H]chromen-9-ila (61)	*C. longifolius*	Petiole [26]	
3-methoxyangelicin (62)	*C. longifolius*	Stem [48]	^{1}H-NMR, ^{13}C-NMR [55]
		Leaves and petiole [26,40,47]	
Pimpinellin (63)	*C. longifolius*	Stem [48]	^{1}H-NMR, ^{13}C-NMR [56]
		Leaves and petiole [26,40,47]	
Sphondin (64)	*C. longifolius*	Stem [48]	^{1}H-NMR, ^{13}C-NMR [56]
		Leaves and petiole [26,40,47]	
Isobergapten (65)	*C. longifolius*	Stem [26]	^{1}H-NMR, ^{13}C-NMR [56]
3,6-dimethoxyangelicin (66)	*C. longifolius*	Stem and leaves [26,40]	^{1}H-NMR [55]

* Data not found

seen with a chemical shift around δ_H 7.40, characteristic of the region of aromatic hydrogens, referring to hydrogen H-5, when its neighboring carbon (C-6) is not substituted. However, if the C-6 carbon has a methoxyl substituent, as in **52** and **54**, the sign of H-5 in the ^{1}H NMR spectrum is represented by a singlet with a shift below δ_H 7.00 due to the effect of the carbon donor group electrons (OCH_3) when in the *ortho*-position.

Pyranocoumarins are represented by compounds **56** and **59**, compound **56** being a linear pyranocoumarin, and compound **59** an angular pyranocoumarin, in which no data were found in the literature on the chemical shifts of hydrogen. For compound **56**, the patterns of chemical shift values of H-3, H-4, and H-5 follow the same example as the basic coumarins, as explained in the paragraphs above. In H-3' hydrogen, the triplet chemical shift value is increased, due to bonding with a hydroxyl group; and the methyls at C-2' have δ_H values above the average for this group, around δ_H 1.30 ppm, because they are close to oxygen.

Coumarins **57** and **58** are classified as linear furanocoumarins because they have a five-membered heterocyclic ring linearly linked to the basic coumarin. They demonstrate the same representative signals of coumarins on hydrogens H-3, H-4, and H-5. Compound **7** did not show ^{1}H NMR data in the reported literature.

Compounds **60-66** isolated from *Conchocarpus* are angular furanocoumarins as they have the furan ring conjugated at carbons C-7 and C-8. Thus, the C-8 carbon becomes quaternary and does not show a hydrogen signal, unlike the other coumarins. It is important to note that the chemical shift value of H-4 is above δ_H 8.00 in **63** and **65**, as a result of the replacement of an oxygenated group at C-5. Furthermore, **62** and **66** do not show H-3 hydrogen signals due to a methoxyl substitution; and this is confirmed with the decrease in the chemical shift value of H-4 by the electron donating effect of the substituent group (OCH_3) in H-3.

Still on angular furanocoumarins, the signals of hydrogens H-2' and H-3' are observed with values in the region of aromatic hydrogens, and H-3' presents a smaller chemical shift in relation to H-2', due to the effect of resonance between the electron pair of oxygen and the double bond of the furan ring, leaving the highest electronic density close to H-3', and consequently, lowering the value of its chemical shift.

The ^{13}C NMR signals of the substances in this review are predictable according to the groups belonging to the

Table 5. ^{1}H-NMR data (in $CDCl_3$) of coumarins from *Conchocarpus* species. (Multiplicities, *J*, in parenthesis)

H	Compound/δ_H (ppm), J_H (Hz)					
	52	**53**	**54**	**55**	**56**	
3	6.27 (*d*, 9.5)	6.16 (*d*, 10.0)	6.23 (*d*, 9.5)	6.18 (*d*, 9.3)	6.18 (*d*, 9.4)	
4	7.60 (*d*, 9.5)	7.87 (*d*, 9.1)	7.59 (*d*, 9.5)	7.64 (*d*, 9.3)	7.58 (*d*, 9.4)	
5	6.93 (*s*)	7.50 (*d*, 9.1)	6.83 (*s*)	7.35 (*d*, 9.5)	6.70 (*s*)	
6		6.83 (*dd*, 2.7; 8.2)		6.80 (*dd*, 2.1; 8.4)		
8	6.85 (*s*)	6.74 (*d*, 2.7)	6.78 (*s*)	6.77 (*d*, 2.1)	7.21 (*s*)	
1'				4.51 (*d*, 6.7)		
2'				5.41 (*t*, 6.7)		
3'					4.73 (*t*)	
4'				2.00 (*m*)	3.22 (*dd*, 6.1)	
5'				2.00 (*m*)		
6'				5.05 (*m*)		
6-OCH_3	3.96 (*s*)		3.90 (*s*)			
7-OCH_3			3.88 (*s*)			
2'-CH_3					1.27 (*s*); 1.37 (*s*)	
3'-OCH_3				1.60 (*s*)		
7'- OCH_3				1.76 (*s*)		
H	**Compound/δ_H (ppm), J_H (Hz)**					
	57	**62**	**63**	**64**	**64**	**66**
3	6.22 (*d*, 9.4)		6.36 (*d*, 9.8)	6.39 (*d*, 9.6)	6.31 (*d*, 9.8)	
4	7.60 (*d*, 9.4)	6.95 (*s*)	8.07 (*d*, 9.8)	7.76 (*d*, 9.5)	8.16 (*d*, 9.8)	6.90 (*s*)
5	7.22 (*sl*)	7.29 (*d*, 8.9)		6.78 (*s*)		6.75 (*s*)
6		7.41 (*dd*, 8.9; 0.8)			6.89 (*s*)	
8	6.75 (*s*)					
2'	4.74 (*dd*, 9.2; 8.5)	7.65 (*d*, 2.2)	7.65 (*d*, 2.2)	7.70 (*d*, 2.0)	7.57 (*d*, 2.3)	7.73 (*d*, 2.2)
3'a	3.22 (*ddd*, 14.8; 8.5; 1.0)	7.05 (*dd*, 2.2; 0.8)	7.07 (*d*, 2.2)	7.12 (*d*, 2.1)	7.02 (*d*, 2.3)	7.07 (*d*, 2.2)
3'b	3.20 (*ddd*, 14.8; 9.2; 1.0)					
2"	1.38 (*s*)					
3"	1.24 (*s*)					
3-OCH_3		3.98 (*s*)				3.95 (*s*)
5- OCH_3			4.03 (*s*)		3.97 (*s*)	
6-OCH_3			4.14 (*s*)	4.04 (*s*)		4.07 (*s*)

basic structure of coumarins, such as the ester carbonyl that signals at around δ_C 160.0 ppm, as well as the carbons C-3 to C-10 corresponding to aromatic ring carbons. Carbons C-7 and C-9 present high values due to the presence of oxygen, which is an electronegative group, as a neighbor. In addition, there is an increase in the value of the C-2' carbon because it is an sp^2 carbon and is directly linked to the electronegative group, suffering a great deshielding effect.

4. Conclusion

The objective of this work was to emphasize a review of the ^{1}H and ^{13}C NMR spectral data of alkaloids and coumarins from *Conchocarpus* species, and although there are not many studies on this genus, it is possible to verify the importance of these classes of secondary metabolites in this genus, containing 51 isolated alkaloids and 15 isolated coumarins. Some spectral data were not found in the literature, however, the values of the chemical positions obtained from the mentioned sources are consistent with the particularity of each hydrogen and carbon, observing the predictability of the chemical positions in view of the group or the effect that acts on the molecular structure. We anticipate that this review will contribute to future chemical studies of *Conchocarpus* species, as knowing the chemical

Table 6. ^{13}C-NMR data (in $CDCl_3$) of coumarins from *Conchocarpus* species

C	Compound/δ_C (ppm)					
	52	**53**	**54**	**55**	**56**	
2	161.3	160.5	161.4	161.0	162.1	
3	113.3	112.0	113.4	112.0	111.6	
4	143.2	144.2	143.3	144.0	142.6	
5	107.4	129.7	108.0	128.5	96.8	
6	143.9	113.2	146.3	113.1	154.5	
7	144.3	161.6	152.8	162.0	124.0	
8	103.1	102.5	100.0	101.5	111.6	
9	149.6	156.2	150.0	155.5	160.4	
10	111.4	111.9	111.4	112.2	124.0	
1'				65.4		
2'				118.2	90.1	
3'				142.1	70.5	
4'				39.4	28.4	
5'				26.1		
6'				123.5		
7'				131.7		
8'				25.6		
6-OCH_3	56.3		56.4			
7-OCH_3			56.4			
2'-CH_3					23.2; 25.0	
3'-OCH_3				17.3		
7'-OCH_3				16.4		

C	Compound/δ_C (ppm)					
	57	**59**	**62**	**63**	**64**	**65**
2	161.1	159.9	157.7	160.8	161.1	161.1
3	112.3	113.2	143.0	113.7	114.7	110.2
4	139.4	143.3	113.9	139.9	144.4	140.0
5	123.4	129.2	122.4	143.2	104.0	154.4
6	125.0	114.5	108.9	135.1	143.2	90.7
7	163.3	156.5	155.3	149.8	143.3	158.1
8	97.9	106.8	113.8	114.0	118.8	110.2
9	155.7	154.5	143.1	144.4	147.2	148.9
10	113.7	112.6	116.5	109.4	113.8	106.0
2'	91.1	77.5	147.7	145.4	146.1	144.5
3'	29.5	72.0	103.7	104.3	104.7	104.1
4'		63.9				
5'		24.1				
6'		22.8				
1"	71.6					
2"	26.2					
3"	24.2					
3-OCH_3			56.2			
5-OCH_3				61.2		56.5
6-OCH_3				62.4	56.7	
C=O (Ac)		169.7				
CH_3 (Ac)		20.7				

composition of this genus facilitates the identification of new structures.

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Bibliographic References

1. Afonso, L. F.; *Dissertação de Mestrado,* Universidade de São Paulo, 2018. [Link]
2. Morton, C. M.; Telmer, C.; New Subfamily Classification for

the Rutaceae. *Annals of the Missouri Botanical Garden* **2014**, *99*, 620. [Crossref]

3. Groppo, M.; Lemos, L. J. C. de; Ferreira, P. de L.; Ferreira, C.; Bruniera, C. P.; Castro, N. M. de; Pirani, J. R.; Ottra, J. H. L. el; Kallunki, J. A.; A tree nymph of the Brazilian Atlantic Forest: Dryades (Galipeinae, Rutaceae), a new neotropical genus segregated from *Conchocarpus*. *Molecular phylogenetics and evolution* **2021**, *154*, 106971. [Crossref][PubMed]
4. Saraiva Filho, D. E.; Sousa, J. B. D.; Santos, H. S. D.; Fontenelle, R. O. D. S.; Compostos químicos isolados de extratos e óleos essenciais do gênero *Zanthoxylum Linnaeus* (Rutaceae) e seu potencial antimicrobiano. *Hoehnea* **2020**, *47*. [Crossref]
5. Appelhans, M. S.; Bayly, M. J.; Heslewood, M. M.; Groppo, M.; Verboom, G. A.; Forster, P. I.; Kallunki, J. A.; Duretto, M. F.; A new subfamily classification of the *Citrus* family (Rutaceae) based on six nuclear and plastid markers. *Taxon* **2021**, *70*, 1035. [Crossref]
6. Groppo, M.; Afonso, L. F.; Pirani, J. R.; A review of systematics studies in the Citrus family (Rutaceae, Sapindales), with emphasis on American groups. *Brazilian Journal of Botany* **2022,** *45*, 181. [Crossref]
7. Cabral, R. S.; Allard, P. M.; Marcourt, L.; Young, M. C. M.; Queiroz, E. F.; Wolfender, J. L.; Targeted Isolation of Indolopyridoquinazoline Alkaloids from *Conchocarpus fontanesianus* Based on Molecular Networks. *Journal of natural products* **2016**, *79*, 2270. [Crossref][PubMed]
8. Isidoro, M. M.; Silva, M. F. d. G. F. d.; Fernandes, J. B.; Vieira, P. C.; Arruda, A. C.; Silva, S. d. C.; Fitoquímica e quimiossistemática de *Euxylophora paraensis* (Rutaceae). *Química Nova* **2012**, *35*, 2119. [Crossref]
9. Dewick, P. M.; *Medicinal Natural Products: A Biosynthetic Approach*; 2a. ed., Wiley & Sons: London, 2002.
10. Kaur, R.; Arora, S.; Alkaloids-important therapeutic secondary metabolites of plant origin. *Journal of Critical Reviews* **2015**, *2*, 1. [Link]
11. Andrade, M. R. d.; *Tese de Doutorado*, Universidade Federal de São Carlos, 2003. [Link]
12. Waterman, P. G.; Alkaloids of the rutaceae: their distribution and systematic significance. *Biochemical Systematics and Ecology* **1975**, *3*, 149. [Crossref]
13. Kukula-Koch, W. A.; Widelski, J.; Em *Alkaloids;* Badal, S.; Delgoda, R., eds.; Academic Press: Boston, 2017, cap. 9. [Crossref]
14. Roberts, M. F.; *Alkaloids: Biochemistry, Ecology, and Medicinal Applications*; 1a. ed., Springer Science & Business Media: Springer US, 1998.
15. Franco, D.; Pereira, T.; Vitorio, F.; Nadur, N.; Lacerda, R.; Kümmerle, A; A importância das cumarinas para a química medicinal e o desenvolvimento de compostos bioativos nos últimos anos. *Química Nova* **2020**, *44*, 180. [Crossref]
16. Zhu, J.-J.; Jiang, J.-G.; Pharmacological and Nutritional Effects of Natural Coumarins and Their Structure-Activity Relationships. *Molecular nutrition & food research* **2018**, *62*, 1701073. [Crossref]
17. Dias, A. R. d. S. V. G.; *Dissertação de Mestrado*, Instituto Superior de Ciências da Saúde Egas Moniz, 2015. [Link]
18. Oliveira, L. S. S. d.; Araújo, M. F. d.; Braz-Filho, R.; Vieira, I. J. C.; Two New Labdane-type Diterpenoids and others Compounds from *Conchocarpus cyrtanthus* (Rutaceae). *Revista Virtual de Química* **2016**, *8*, 27. [Crossref]
19. Cabral, R. S.; *Dissertação de Mestrado*, Instituto de Botânica da Secretaria do Meio Ambiente, 2011. [Link]
20. Sá, I. C. G. d.; *Dissertação de Mestrado*, Universidade Federal de São Carlos, 2010. [Link]
21. Bellete, B. S.; Sá, I. C. G. d.; Mafezoli, J.; Cerqueira, C. d. N.; Silva, M. F. d. G. F. d.; Fernandes, J. B.; Vieira, P. C.; Zukerman-Schpector, J.; Pirani, J. R.; Fitoquímica e quimiossistemática de *Conchocarpus marginatus* e *C. inopinatus* (Rutaceae). *Química Nova* **2012**, *35*, 2132. [Crossref]
22. Cortez, L. E. R.; Cortez, D. A. G.; Ferreira, A. G.; Vieira, P. C.; Silva, M. F. d. G. F. d.; Fernandes, J. B.; Constituintes químicos de *Almeidea coerulea* (Nees & Mart.) A. St.-Hil. Rutaceae. *Revista Brasileira de Farmacognosia* **2006**, 16, 164. [Crossref]
23. Cabral, R. S.; Allard, P.-M.; Marcourt, L.; Young, M. C. M.; Queiroz, E. F.; Wolfender, J.-L.; Targeted Isolation of Indolopyridoquinazoline Alkaloids from *Conchocarpus fontanesianus* Based on Molecular Networks. *Journal of Natural Products* **2016**, *79*, 2270. [Crossref][PubMed]
24. Ambrozin, A. R. P.; *Tese de Doutorado*, Universidade Federal de São Carlos, 2004. [Link]
25. Ito, A.; Shamon, L. A.; Yu, B.; Mata-Greenwood, E.; Lee, S. K.; Mehta, R. G.; Farnsworth, N. R.; Fong, H. H. S.; Pezzuto, J. M.; Kinghorn, A. D.; Antimutagenic Constituents of *Casimiroa edulis* with Potential Cancer Chemopreventive Activity. *Journal of agricultural and food chemistry* **1998**, *46*, 3509. [Crossref]
26. Facchini, P. H.; *Tese de doutorado*, Universidade de São Carlos, 2005.
27. Chakravarty, A. K.; Sarkar, T.; Masuda, K.; Shiojima, K.; Carbazole alkaloids from roots of *Glycosmis arborea*. *Phytochemistry* **1999**, *50*, 1263. [Crossref]
28. Kang, S. S.; Woo, W. S.; Furoquinoline alkaloids from the leaves of *Melicope confusa*. *Archives of Pharmacal Research* **1986**, *9*, 11. [Crossref]
29. Moulis, C.; Gleye, J.; Fourasté, I.; Stanislas, E.; Nouvelles Furoquinoléines de *Monnieria trifolia*. *Planta Medica* **1981**, *42*, 400. [Crossref][PubMed]
30. Rasulova, K. A.; Bessonova, I. A.; Yagudaev, M. R.; Yunusov, S. Y.; Haplosinine — A new furanoquinoline glycoalkaloid from *Haplophyllum perforatum*. *Chemistry of Natural Compounds* **1987**, *23*, 731. [Crossref]
31. Ambrozin, A. R. P.; Vieira, P. C.; Fernandes, J. B.; Silva, M. F. d. G. F. d.; Albuquerque, S. d.; Piranoflavonas inéditas e atividades tripanocidas das substâncias isoladas de *Conchocarpus heterophyllus*. *Química Nova* **2008**, *31*, 740. [Crossref]
32. Cortez, L. E. R.; *Tese de doutorado,* Universidade de São Carlos, 2002.
33. Cantrell, C. L.; Schrader, K. K.; Mamonov, L. K.; Sitpaeva, G. T.; Kustova, T. S.; Dunbar, C.; Wedge, D. E.; Isolation and Identification of Antifungal and Antialgal Alkaloids from Haplophyllum sieversii. *Journal of Agricultural and Food Chemistry* **2005**, *53*, 7741. [Crossref][PubMed]

34. Alves, I. M.; *Dissertação de Mestrado,* Instituto de Química, 2008. [Link]
35. Campbell, W. E.; Davidowitz, B.; Jackson, G. E.; Quinolinone alkaloids from an Agathosma species. *Phytochemistry* **1990**, *29*, 1303. [Crossref]
36. Cortez, D. A. G.; Cortez, L. E. R.; B. Fernandes, J.; Vieira, P. C.; Ferreira, A. G.; Silva, M. F. d. G. F. d.; New Alkaloids from Conchocarpus gaudichaudianus. *Heterocycles* **2009**, *78*, 2053. [Crossref]
37. Bellete, B. S.; *Dissertação de Mestrado,* Universidade Federal de São Carlos, 2013. [Link]
38. Albarici, T. R.; *Tese de Doutorado,* Universidade Federal de São Carlos, 2006. [Link]
39. Velozo, E. d. S.; *Tese de Doutorado*, Universidade de São Carlos, 1995
40. Mafezoli, J.; *Tese de Doutorado*, Universidade de São Carlos, 2001.
41. Spatafora, C.; Tringali, C.; Bioactive Metabolites from the Bark of *Fagara macrophylla*. *Phytochemical Analysis: An International Journal of Plant Chemical and Biochemical Techniques* **1997**, *8*, 139. [Crossref]
42. Naidoo, D.; Coombes, P. H.; Mulholland, D. A.; Crouch, N. R.; van den Bergh, A. J. J.; N-Substituted acridone alkaloids from *Toddaliopsis bremekampii* (Rutaceae: Toddalioideae) of south-central Africa. *Phytochemistry* **2005**, *66*, 1724. [Crossref] [PubMed]
43. Bergenthal, D.; Mester, I.; Rózsa, Z.; Reisch, J.; ^{13}C-NMR-spektren einiger acridon-alkaloide. *Phytochemistry* **1979**, *18*, 161. [Crossref]
44. Atangana, A. F.; Toze, F. A. A.; Langat, M. K.; Happi, E. N.; Mbaze, L. L. M.; Mulholland, D. A.; Waffo, A. F. K.; Sewald, N.; Wansi, J. D.; Acridone alkaloids from *Vepris verdoorniana* (Excell & Mendonça) Mziray (Rutaceae). *Phytochemistry Letters* **2017**, *19*, 191. [Crossref]
45. Vieira, P. C.; Kubo, I.; Kujime, H.; Yamagiwa, Y.; Kamikawa, T.; Molluscicidal Acridone Alkaloids from *Angostura paniculata*: Isolation, Structures, and Synthesis. *Journal of natural products* **1992**, *55*, 1112. [Crossref][PubMed]
46. Hu, C. Q.; Li, K. K.; Yang, X. W.; New glycosidic alkaloid from the nearly ripe fruits of *Euodia rutaecarpa*. J*ournal of Asian natural products research* **2012**, *14*, 634. [Crossref][PubMed]
47. Magalhães, C. M. I.; *Dissertação de Mestrado*, Instituto de Biociências, Rio Claro, 2001.
48. Godoy, M. d. F. P.; *Dissertação de Mestrado,* Universidade Estadual Paulista (UNESP), 2003. [Link]
49. Paula, V. F. D.; Barbosa, L. C. D. A.; Piló-Veloso, D.; Demuner, A. J.; Howarth, O.; Constituintes químicos da casca de *Ochroma lagopus* swartz (Bombacaceae). *Ecletica Química* **1998**, *23*, 45. [Crossref]
50. Mazimba, O.; Umbelliferone: Sources, chemistry and bioactivities review. *Bulletin of Faculty of Pharmacy, Cairo University* **2017**, *55*, 223. [Crossref]
51. Vila-Nova, N. S.; Morais, S. M.; Falcão, M. J. C.; Bevilaqua, C. M. L.; Rondon, F. C. M.; Wilson, M. E.; Vieira, I. G. P.; Andrade, H. F.; Leishmanicidal and cholinesterase inhibiting activities of phenolic compounds of *Dimorphandra gardneriana* and *Platymiscium floribundum*, native plants from Caatinga biome. *Pesquisa Veterinária Brasileira* **2012**, *32*, 1164. [Crossref]
52. Silva, C. V. d.; Detoni, C. B.; Velozo, E. d. S.; Guedes, M. L. d. S.; Alcalóides e outros metabólitos do caule e frutos de *Zanthoxylum tingoassuiba* A. St. Hil. *Química Nova* **2008**, *31*, 2071. [Crossref]
53. Razavi, S. M.; Imanzadeh, G.; Jahed, F. S.; Zarrini, G.; Pyranocoumarins from *Zosima absinthifolia* (Vent) link roots. *Russian Journal of Bioorganic Chemistry* **2013**, *39*, 215. [Crossref] [PubMed]
54. Macías, F. A.; Massanet, G. M.; Rodríguez-Luis, F.; Salvá, J.; Fronczek, F. R.; ^{13}C NMR of coumarins. II—Khellactones: Spectroscopic criteria to establish the relative configuration of the dihydropyran ring. *Magnetic Resonance in Chemistry* **1989**, *27*, 653. [Crossref]
55. Müller, A. H.; Degáspari, L. R. O.; Vieira, P. C.; da Silva, M. F. D. G. F.; Fernandes, J. B.; Pirani, J. R.; 3-Methoxyfurocoumarins from *Pilocarpus riedelianus*. *Phytochemistry* **1993**, *34*, 585. [Crossref]
56. O'Neill, T.; Johnson, J. A.; Webster, D.; Gray, C. A.; The Canadian medicinal plant *Heracleum maximum* contains antimycobacterial diynes and furanocoumarins. *Journal of ethnopharmacology* **2013**, *147*, 232. [Crossref][PubMed]
57. Alvarenga, E. S.; Pinto, B. N. S.; Santos, A. R.; Oliveira, W. F.; de Paula, V. F.; Oliveira, M. N.; Junior, J. M. B.; Batista, A. N. d. L.; Structural elucidation by NMR assisted by DFT calculations of a novel natural product from *Conchocarpus mastigophorus* (Rutaceae). *Asian Journal of Organic Chemistry* **2022**. [Crossref]
58. Min, Y. D.; Kwon, H. C.; Yang, M. C.; Lee, K. H.; Choi, S. U.; Lee, K. R. Isolation of limonoids and alkaloids from *Phellodendron amurense* and their multidrug resistance (MDR) reversal activity. *Archives of pharmacal research* **2007**, *30*, 58. [Crossref][PubMed]
59. Ju-ichi, M.; Kaga, H.; Muraguichi, M.; Inoue, M.; Kajiura, I.; Omura, M.; Furukawa, H.; New Acridone Alkaloid and Coumarin from *Citrus* Plants. *Heterocycles* **1988**, *27*, 2197. [Crossref]
60. Kumar, S.; Raj, K. Khare, P.; Flavones and acridones from *Atalantia wightii*. *Indian Journal of Chemistry* **2009**, *48B*, 291. [Link]
61. Wu, T., Furukawa, H., Kuoh, C., Huo, K.; Acridone alkaloids. Part 9. Chemical constituents of *Glycosmis citrifolia* (Willd.) Lindl. Structures of novel linear pyranoacridones, furoacridones, and other new acridone alkaloids. *Journal of the Chemical Society*, *Perkin Transactions 1* **1983**, 1681. [Crossref]
62. Wu, T.; Furukawa, H. Acridone alkaloids. VII. Constituents of *Citrus sinensis* Osbeck var. *brasiliensis* Tanaka. Isolation and characterization of three new acridone alkaloids, and a new coumarin. *Chemical & Pharmaceutical Bulletin* **1983**, *31*, 901. [Crossref]