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Article

20(*R*)- and 20(*S*)-Simarolide Epimers Isolated from *Simaba cuneata* - Chemical Shifts Assignment of Carbon and Hydrogen Atoms

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Os quassinóides C_{25} 20(*R*)- e 20(*S*)-simarolídeo foram isolados de *Simaba cuneata*, Simaroubaceae. As estruturas destas substâncias foram caracterizadas por dados espectrais, incluindo espectros de RMN 1D e 2D que foram também usados para a completa atribuição dos deslocamentos químicos dos átomos de carbono e hidrogênio.

The C_{25}-quassinoids 20(*R*)- and 20(*S*)-simarolide were isolated from *Simaba cuneata*, Simaroubaceae. The structures of these two compounds were characterized by spectral data, including 1D and 2D NMR spectra which were also used for the complete assignment of the carbon and hydrogen atom chemical shifts.

Keywords: Simaba cuneata, Simaroubaceae, *C25-quassinoids*

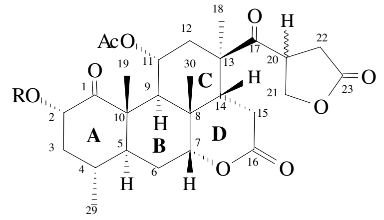
Introduction

20(*R*)-simarolide (**1a**), a C-25 quassinoid was first isolated from *Simarouba amara*. Its structural elucidation, including absolute stereochemistry has already been described in the literature[1,2]. The phytochemical study of a *Simaba cuneata* specimen has allowed the isolation of (**1a**) and its C-20 epimer (**1b**). The characterization of these two quassinoids was based on spectral data analysis, obtained from the diacetylated derivatives **2a** and **2b**, especially NMR [(1D: ^{1}H-NMR, ^{13}C-NMR-PND and ^{13}C-NMR-DEPT) and (2D: ^{1}H x ^{1}H-COSY, ^{1}H x ^{1}H-NOESY, HMQC and HMBC)]. The NMR data comparison of both compounds isolated from *Simaba cuneata* allowed the localization of an acetoxyl group at C-11 (**1a** and **1b,** Table 1), and the correct assignment of the chemical shifts of all hydrogen (δ_H) and 13-carbon (δ_C) atoms of both diacetyl derivatives (**2**), 20(*R*)-2-O-acetylsimarolide (**2a**) and 20(*S*)-2-O-acetylsimarolide (**2b**).

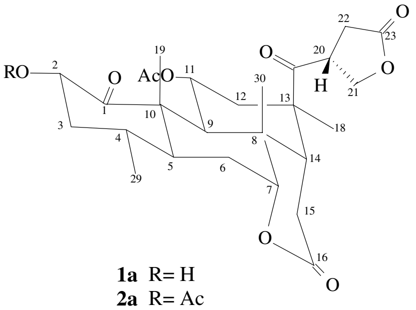
The presence of a carbonyl group at C-17 led us to discuss the possibility of **1b** being the result of a C-20 epimerization (α carbon to the carbonyl group) of the major natural compound 20(*R*)-simarolide (**1a**), during the extraction and isolation processes. However, the bioproduction of 20(*S*)-simarolide still can not be discarded.

Results and Discussion

The ^{13}C-NMR spectra signals of **2a** and **2b** (Table 1) corresponding to quaternary carbons [$(C)_9$: two ketone carbonyls, four ester and lactone carbonyls and three Csp^3 in C-C bonds], methines [$(CH)_8$: three Csp^3 attached to oxygen and five Csp^3 involved in C-C bonds], methylenes [$(CH_2)_6$: one Csp^3 attached to oxygen and five Csp^3 involved in C-C bonds] and methyls [$(CH_3)_6$: four involved in C-C bonds and two attached to Csp^2 carbonyl carbon] were identified by the comparative analysis of the hydrogen decoupling spectra (PND = proton noise decoupling) and by the DEPT technique (Distortionless Enhancement by Polarization Transfer, θ = 90°: only CH signals; θ = 135°: CH_2 signals in opposite phase to CH and CH_3; after the removal of these signals from the PND spectra, the quaternary carbon signals were obtained)[3]. Based on small chemical shift differences observed between **2a** and **2b** we suggested that they were diastereomers.



1 R= H
2 R= Ac



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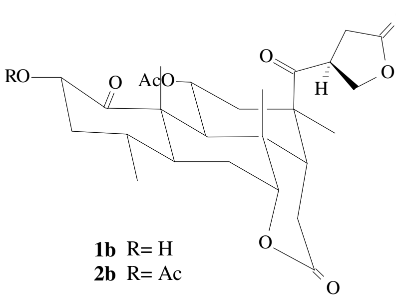
2a R= Ac



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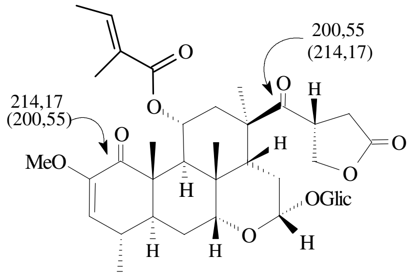
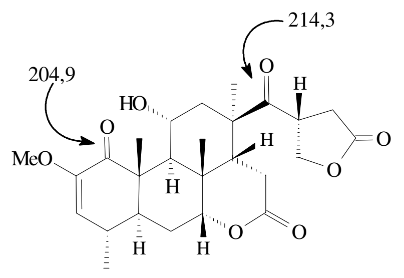
2b R= Ac



3 (correct assignment in bracket)



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The number of functional groups {two carbonyl ketones (**2a**: δ_C 211.90, C-17 and 206.60, C-1; **2b**: δ_C 211.96, C-17 and 206.66, C-1), two acetoxyls [**2a**: δ_C 169.94 and 20.58; δ_H 2.13 (AcO-2); δ_C 171.66 and 21.03; δ_H 2.04 (AcO-11); **2b**: δ_C 170.01 and 20.64; δ_H 2.13 (AcO-2); δ_C 171.73 and 21.09; δ_H 2.04 (AcO-11)], one γ-lactone [**2a**: δ_C 174.45 (C-23); **2b**: δ_C 174.50 (C-23)], one δ-lactone [**2a**: δ_C 169.25 (C-16); **2b**: δ_C 169.31 (C-16)] and the remaining quaternaries carbons [**2a**: $(C)_3$; **2b** $(C)_3$], methine [**2a**: $(CH)_8$; **2b**: $(CH)_8$], methylene [**2a**: $(CH_2)_6$; **2b**: $(CH_2)_6$] and methyls remaining [**2a**: $(CH_3)_4$; **2b**: $(CH_3)_4$]}, combined with the δ_C and δ_H and the multiplicity of the hydrogen atom signals observed in the ^{1}H-NMR spectra (1D and 2D ^{1}H x ^{1}H-COSY), have allowed the structure of simarolide (**1a**), a quassinoid with twenty five carbon atoms (C_{25}) isolated from *Simarouba amara*[1] to be proposed. The relative stereochemistry of **1a** was defined on the basis of X-ray analysis[1,2]. This is the first report of the complete NMR carbon and hydrogen assignment of **1a**.

The ^{1}H-NMR (Table 2) and ^{1}H x ^{1}H-COSY of **2a** and **2b** revealed small significant differences for the protons H-20 [**2a**: δ_H 4.31 (*m*); **2b**: δ_H 4.30 (*m*)] and CH_2-21 [**2a**: δ_H 4.59 (*t*, J = 7.2 Hz) and 4.30 (*m*); **2b**: δ_H 4.60 (*t*, J = 7.6 Hz) and 4.34 (*m*)], clearly showing different spectral patterns (Figure 1 and 2). These differences were confirmed by the comparison (Figure 3 and 4) of the heteronuclear correlation spectra (HMQC)[4,5] of **2a** and **2b** (two epimers at C-20), which revealed the δ_C CH-20 [**2a**: δ_C/ δ_H 41.50 (CH-20)/4.31 (*m*, H-20); **2b**: δ_C/ δ_H 41.58 (CH-20)/4.30 (*m*, H-20)] and CH_2-21 [**2a**: δ_C/ δ_H 70.26 (CH_2-21)/4.59 (*t*, H-21) and 4.30 (*m*, H-21b); **2b**: δ_C/ δ_H 70.22 (CH-21)/4.60 (*t*, H-21a) and 4.34 (*m*, H-21b)] and have permitted the observation of distinct chemical shifts for H-20 (δ_H 4.31) in **2a** and (δ_H 4.30) in **2b**, and for H-21 (δ_H 4.30) in **2a** and (δ_H 4.34) in **2b**. Therefore, it was possible to deduce that the two acetylated derivatives **2a** and **2b** differ only in the stereochemistry of the chiral carbon C-20. From HMQC spectra of **2a** and **2b** it was possible to assign all chemical shifts for both, hydrogen and hydrogenated carbon atoms (Tables 1 and 2), also establishing the δ_H observed for CH-20 (**2a**: δ_H 4.31 (*m*); **2b**: δ_H 4.30), which is surprising for a methine hydrogen occupying the α position in relation to the carbonyl group, since the δ_C [**2a**: δ_C 41.50 (CH-20); **2b**: δ_C 41.58 (CH-20)] revealed to be compatible with the parameters expected for δ_C in these structural conditions[3].

The unequivocal assignment of the δ_C of all **2a** carbon atoms (Table 1) was assured by the analysis of the heteronuclear correlation bidimensional spectrum, HMBC. Therefore, for example, the spin-spin interactions of C-1 (δ_C 206.60) with the 3H-19 [δ_H 1.24 (Table 2), $^3J_{CH}$] and C-17 (δ_C 211.90) with the H-12ax [δ_H 1.69 (Table 2), $^3J_{CH}$] and the 3H-18 [δ_H 0.98 (Table 2), $^3J_{CH}$] have allowed the correct assignment of the chemical shifts for C-1 and C-17. Other long range correlations can be found in Table 1. Based on the correct assignment of C-1 (δ_C 206.60) and C-17 (δ_C 211.90), it was possible to reassign the chemical shifts for this structure and correct some data from the literature. So, the assignment of the δ_C of C-1 (δ_C 214.17) and C-17 (numbered as C-22 in reference 6: δ_C 200.55) of the quassinoid (**3**) isolated from *Picrasma javanica*[6] should be corrected to C-1 (δ_C 200.55) and C-22 = C-17 (δ_C 214.17), as observed in the quassinoid (**4**) isolated from *Picrasma ailanthoides*[7], since a solvent (pyridine-d_5) effect should not be responsible for such a modification. The comparison of the ^{13}C-NMR chemical shift for **2a** and **2b** also permitted the correct assignment of the **2b** quaternary carbon δ_C (Table 1).

Table 1. ^{13}C-NMR data (100 MHz) of **2a** and **2b**, obtained from 1D (PND and DEPT) and 2D spectra (HMBC) registered in $CDCl_3$, chemical shifts in δ_C in relation to internal reference TMS*.

	2a			**2b**
		HMBC		
C	δ_C	$^2J_{CH}$	$^3J_{CH}$	δ_C
1	206.60		3H-19	206.66
8	36.76	3H-10	H-11	36.83
10	49.22	H-9, 3H-19		49.29
13	51.36	3H-18		51.43
16	169.25		H-7, H-14	169.31
17	211.90		H-12ax, 3H-18	211.96
23	174.45	H-22	H-21a	174.50
AcO-2	169.94	2.13	H-2	170.01
AcO-11	171.66	2.04	H-11	171.73
CH				
2	72.40	H-3ax		72.46
4	28.61	3H-29		28.69
5	46.61		H-7, 3H-19, 3H-29	46.66
7	81.57		3H-30	81.63
9	36.09		3H-19, H-7	36.16
11	67.59	H-9, H-12ax		67.41
14	43.50	H-15	H-7, 3H-18, 3H-30	43.56
20	41.50	H-22		41.58
CH_2				
3	41.98	H-2	3H-29	42.04
6	26.12			26.21
12	36.33		3H-18	36.44
15	28.56	H-14		28.62
21	70.26	H-20		70.22
22	33.84		2H-21	33.94
CH_3				
18	24.14			24.34
19	13.01		H-9	13.09
29	18.45			18.51
30	23.34		H-9	23.49
AcO-2	20.58			20.64
AcO-11	21.03			21.09

* The data obtained from HMBC spectra was also used in the assignment of these δ_C. The hydrogen atoms δ_H corresponding to the hydrogenated carbons (CH, CH_2 and CH_3) are described in Table 2.

With the unequivocal assignment of the δ_H for **2a** and **2b** through analysis of the HMQC spectrum (Tables 1 and 2), the homonuclear correlation ^{1}H x ^{1}H-COSY has allowed the recognition of all spin-spin interactions of the hydrogen atoms, especially CH-20, CH_2-21 and CH_2-22 (Fig. 1). The spectrum of **2a** revealed, not only the vicinal interactions, but also the coupling of H-21a [δ_H 4.59 (*t*)] in W or M (zig-zag)[5] with H-22 [δ_H 2.75 (*m*)], which was not observed in the spectrum of **2b** (Fig. 1). This comparative analysis allowed the suggestion that the γ-lactone ring in **2a** adopts a conformation in which the spin-spin coupling through *syn* periplanar four bonds with H-21a and H-22 is possible in a W or M geometry ($^4J_{w\text{-}H,H}$), not observed in **2b**. The conformational behavior differences of the γ-lactone ring on both epimers (**2a** and **2b**) can only be justified by a steric interference involving the C-ring and the CH_3-18 and CH_3-30 methyl groups. In fact, the most significant differences in the interatomic distances (Table 3), measured at the minimum energy conformation (**2a**: 102.95 kcal/mol; **2b**: 100.49 kcal/mol) using the molecular modeling program - PCMODEL (version 3.0), involve H-20 and 3H-18 hydrogen atoms (**2a**: 3.867, 4.230, 5.120 Å, with a mean approximated value = 4.406 Å; **2b**: 2.363, 3.583, 3.746 Å, with a mean approximated value = 3.231 Å); ΔÅ = 4.406 - 3.231 = 1.175 Å) and 2H-12 hydrogen atoms (**2a**: 3.804 and 5.000 Å, with a mean approximated value = 4.402 Å; **2b**: 1.880 and 3.447 Å, with a mean approximated value = 2.663 Å; ΔÅ = 4.402 - 2.663 = 1.739 Å). These data were employed to show, as foreseen, that the epimerization of the CH-20

Table 2. ^{1}H-NMR data (400 MHz) of **1** (**1a** + **1b**), **2a** and **2b**, obtained from spectra registered in $CDCl_3$ and TMS as internal reference. Chemical shift in δ and coupling constants (between brackets) in Hz*.

H	**1**	**2a**	**2b**
2	4.68 (*m*)	5.56 (*dd,* J = 7.2 e 12.0)	5.56 (*dd,* J = 7.6 e 12.4)
3	2.52-2.43 (*m*)	2.32 (*m*)	2.33 (*m*)
	1.43 (*m*)	1.46 (*m*)	1.47 (*m*)
4	1.95-1.85 (*m*)	2.05 (*m*)	2.04 (*m*)
5	1.55 (*m*)	1.47 (*d,* J = 12.4)	1.48 (*d,* J = 12.4)
6	1.95-1.85 (*m*)	1.96 (*td,* J = 3.6 e 14.8)	1.96 (*td,* J = 3.6 e 14.8)
	1.73 (*m*)	1.76 (*ddd,* J = 2.0; 12.4 e 14.8)	1.75 (*ddd,* J = 2.0; 12.4 e 14.8)
7	4.15 (*sl*)	4.18 (*sl*)	4.17 (*sl*)
9	2.81 (*d,* J = 11.2)	2.78 (*d,* J = 11.6)	2.78 (*d,* J = 11.6)
11	4.92 (*dt,* J = 11.6 e 4.0)	4.94 (*dt,* J = 11.6 e 4.0)	4.92 (*dt,* J = 11.6 e 4.0)
12	2.52-2.43 (*m*)	2.49 (*dd,* J = 4.0 e 14.0)	2.49 (*dd,* J = 4.0 e 14.8)
	1.69 (*m*)	1.69 (*dd,* J = 14.0 e 11.6)	1.69 (*dd,* J = 14.8 e 11.6)
14	2.64 (*m*)[a]	2.63 (*m*)[a]	2.63 (*m*)[a]
15	2.64 (*m*)[a]	2.63 (*m*)[a]	2.63 (*m*)[a]
18	0.98 (*s*)	0.98 (*s*)	0.98 (*m*)
19	1.14 (*s*)	1.24 (*m*)	1.24 (*m*)
20	4.30-4.20 (*m*)	4.31 (*m*)	4.30 (*m*)
21	4.55 (*t,* J = 7.6)	4.59 (*t,* J = 7.2)	4.60 (*t,* J = 7.6)
	4.30-4.20 (*m*)	4.30 (*m*)	4.34 (*m*)
22	2.70-2.55 (*m*)	2.75 (*m*)	2.75 (*m*)
29	0.87 (*d*)	0.95 (*d,* J = 6.8)	0.95 (*d,* J = 6.4)
30	0.88 (*s*)	0.90 (*s*)	0.89 (*s*)
AcO-2		2.13 (*s*)	2.13 (*s*)
AcO-11	1.89 (*s*)	2.04 (*s*)	2.04 (*s*)

* Homonuclear correlation (^{1}H x ^{1}H-COSY) of **2a** and **2b** in bidimensional spectra and Heteronuclear correlation (HMBC) of **2a** and **2b**, HMBC of **2a** and ^{1}H x ^{1}H-NOESY were also used in the assignment of the hydrogen atoms chemical shift (δ_H).

[a] superimposed signals.

chiral carbon produces diastereoisomers with different energies and interatomic differences between H-20 and the hydrogen atoms bonded to carbons placed close to the chiral center.

The ^{1}H x ^{1}H-NOESY dipolar interaction bidimensional spectra of **2a** and **2b** (Table 4) were used to confirm the *trans* junctions of the A/B and B/C rings and *cis* junctions of the B/δ-lactone and C/δ-lactone rings and their corresponding conformations. The interpretation difficulties observed for the spatial interactions (dipolar-dipolar coupling) due especially to the proximity of H-20 and H-21b absorption positions, involving CH-20, CH-21 and 2H-22 hydrogen atoms were attenuated by the calculation of the interatomic distances (Table 3). Therefore, it was possible to assume the existence of NOE's between H-20 (δ_H 4.30) and H-12eq (δ_H 2.49) and 3H-18 (δ_H 0.98) of **2b**, which were not observed in **2a** (Table 3). Furthermore, in the ^{1}H x ^{1}H-NOESY spectrum of **2b**, a dipolar interaction was observed between H-11ax (δ_H 4.92) and H-22 (δ_H 2.75), indicating spatial proximity of these two hydrogen atoms. As in the spectrum of **2a**, the spatial proximity of H-21b (δ_H 4.30) with H-12eq (δ_H 2.49), 3H-18 (δ_H 0.98) and 3H-30 (δ_H 0.90) could also be assumed. These data were used to postulate the configuration 20(*R*)-2-O-acetylsimarolide (**2a**) for the acetylated derivative of the major natural product (**1a**) and 20(*S*)-2-O-acetylsimarolide (**2b**) of the minor natural product (**1b**). This proposal is in agreement with the specific rotation {**2a**: $[\alpha]_D = -14.0°$ (c 0.8, $CHCl_3$); **2b** $[\alpha]_D = -19.2°$ (c 1.48, $CHCl_3$)} and with biogenetic considerations, since *Simarouba amara*[1], *Picrasma javanica*[6], *Picrasma ailanthoides*[7], are bioproducers of C_{25} quassinoids with 20(*R*) carbon, and *Simaba* *cuneata* belongs to the same Simaroubaceae family. This biogenetic consideration reinforces the possibility of **1b** being a product formed by an epimerization reaction that may have occurred during the extraction and isolation process, but still does not definitely rule out its biogenetic origin.

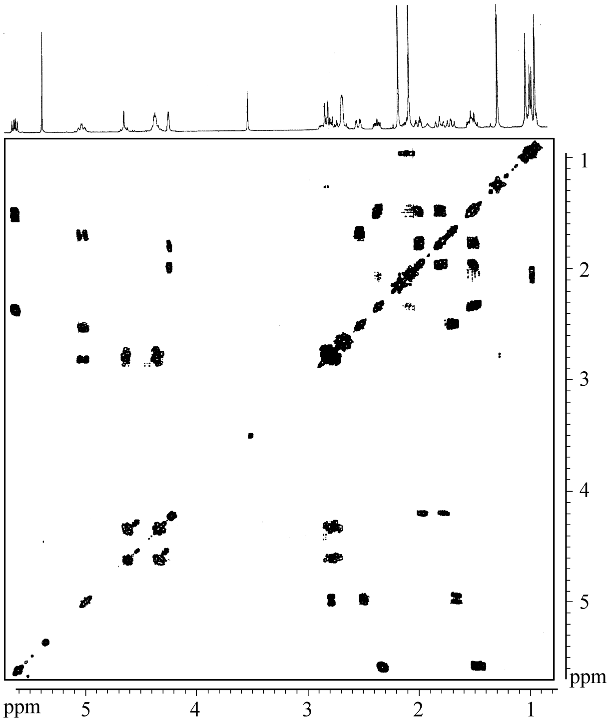


Figure 1. ^{1}H x ^{1}H-COSY spectrum of **2a**.

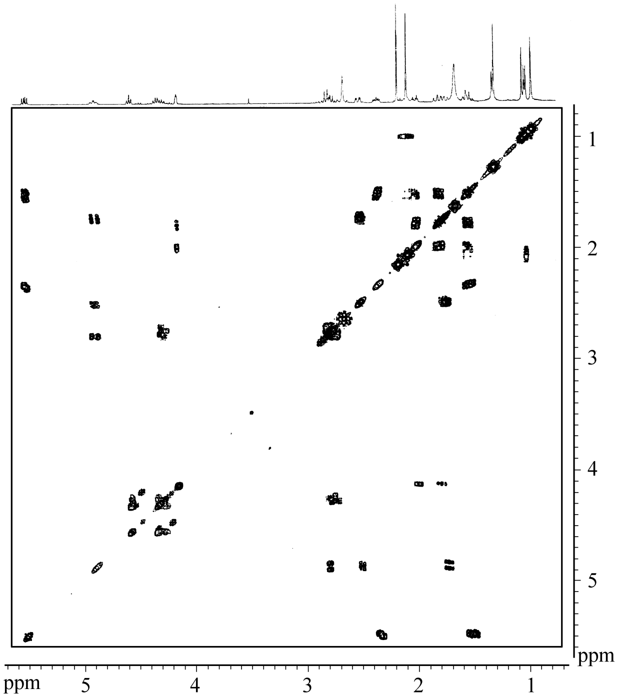


Figure 2. ^{1}H x ^{1}H-COSY spectrum of **2b**.

Finally, the mass spectrum of **2a** and **2b**, obtained by electronic impact at 70 eV, has revealed the peak corresponding to the molecular ion (*m/z* 546, 1%), and the peaks with m/z 486 (29 %) as well as the peaks *m/z* at 427 (7 %) and 426 (16 %) Daltons (M-AcOH – AcO• and/or M-AcO• - AcOH, and M-AcOH-AcOH respectively). Other peaks classified as being important for the structural information can be found summarized in Scheme 1. The analysis of the mass spectrum can also be useful for investigations involving the study of crude extracts by GC/MS[8].

Experimental

General

The melting points were determined in a Microquimica MQRPF-301 digital model equipment with heating plate. The IR spectra were registered on KBr pellets in a Pelkin-Elmer spectrometer. The Bruker ARX-400 model spectrometer (^{1}H: 400 MHz; ^{13}C: 100 MHz) was used to obtain the ^{1}H-NMR and ^{13}C-NMR spectra, using $CDCl_3$ as solvent and TMS as internal reference. The low resolution mass spectra were obtained in a Fisons/Plataform DI/MS 2000 model operating at 70 eV. The specific rotation measurements $[\alpha]_D$ were done in a Perkin-Elmer model 241 digital polarimeter, using 20 s intervals for each reading, averaging a total of ten measurements. For the chromatographic analysis a drop countercurrent chromatograph Eyela DCC-

Table 3. Interatomic distances (Å) of H-20 and other neighbouring hydrogen, measured at the minimum energy conformation of **2a** (102.95 kcal/mol) and of **2b** (100.49 kcal/mol) using the molecular modeling software - PCMODEL.

		2a	**2b**	
H	H	Å	Å	ΔÅ
20	18	3.867	2.363	1.504
		4.230	3.583	0.647
		5.120	3.746	1.374
	21a	3.151	3.108	0.043
	21b	2.544	2.468	0.076
	22a	2.390	2.459	0.069
	22b	3.059	3.098	0.039
	14	5.321	4.490	0.831
	30	6.462	5.290	1.172
		7.079	6.316	0.763
		7.183	6.490	0.693
	15a	4.363	4.946	0.583
	15b	5.103	5.040	0.063
	12a	3.804	1.880	1.924
	12b	5.000	3.447	1.553

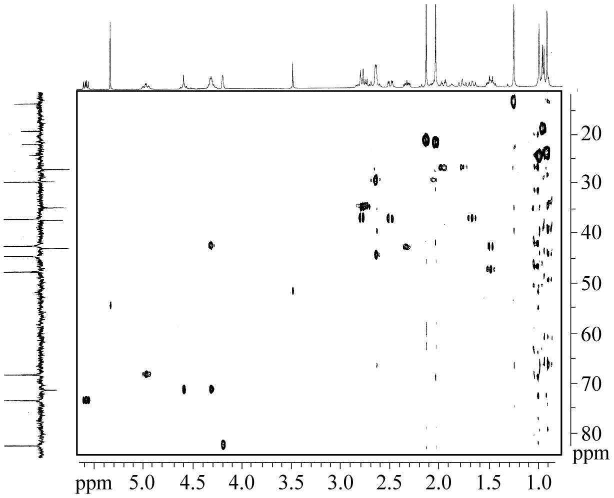


Figure 3. HMQC spectrum of **2a**.

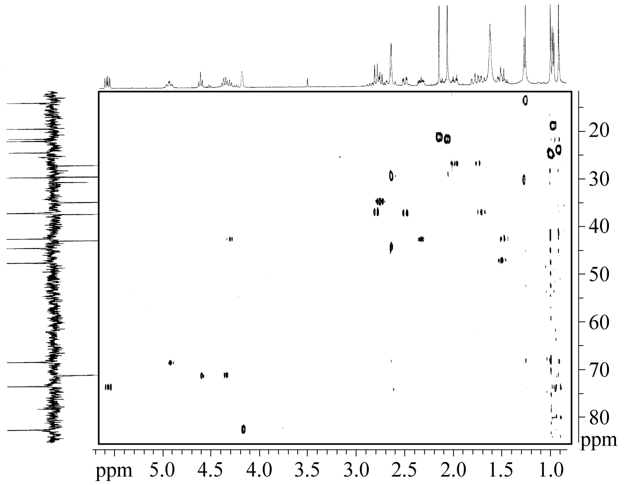
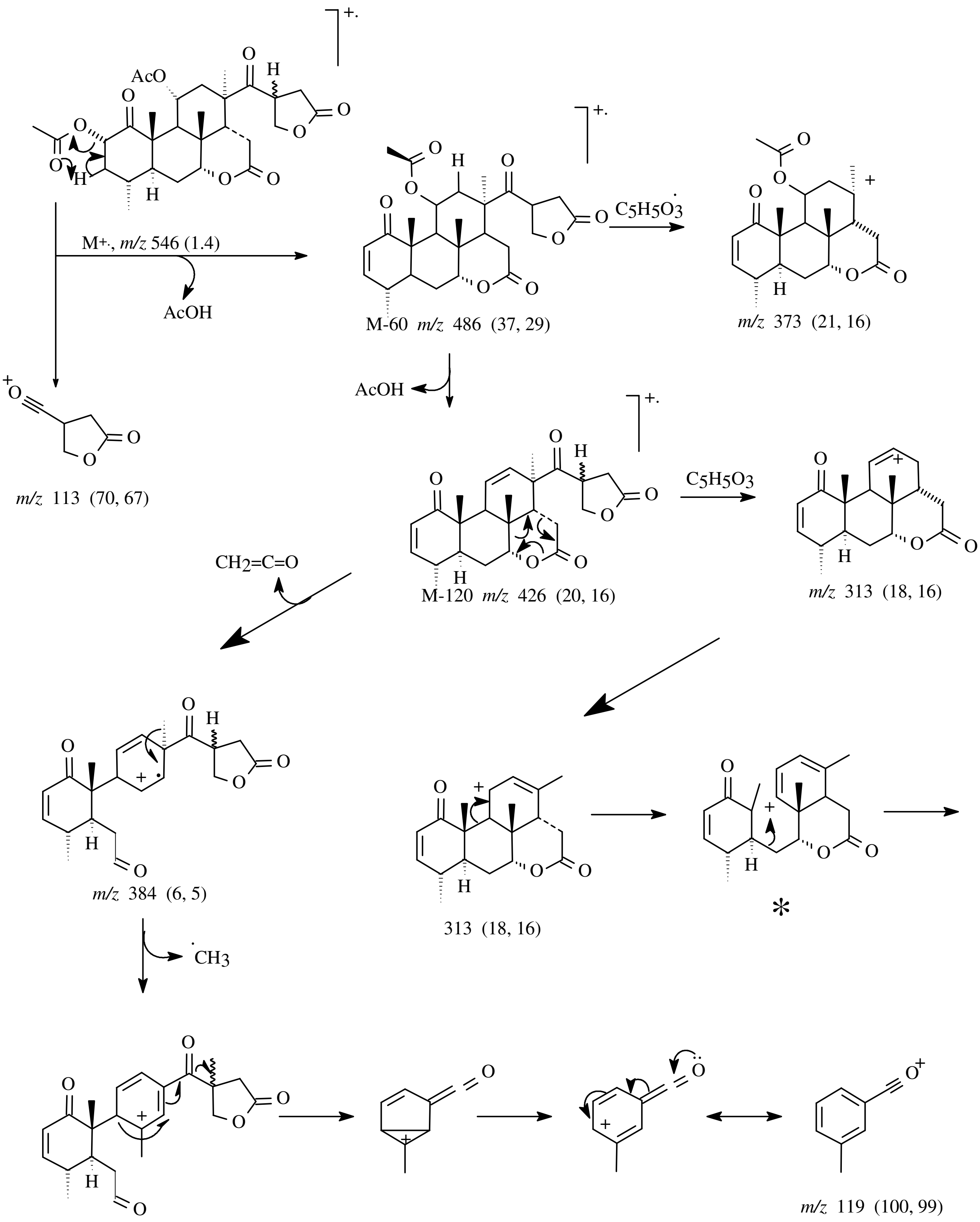


Figure 4. HMQC spectrum of **2b**.

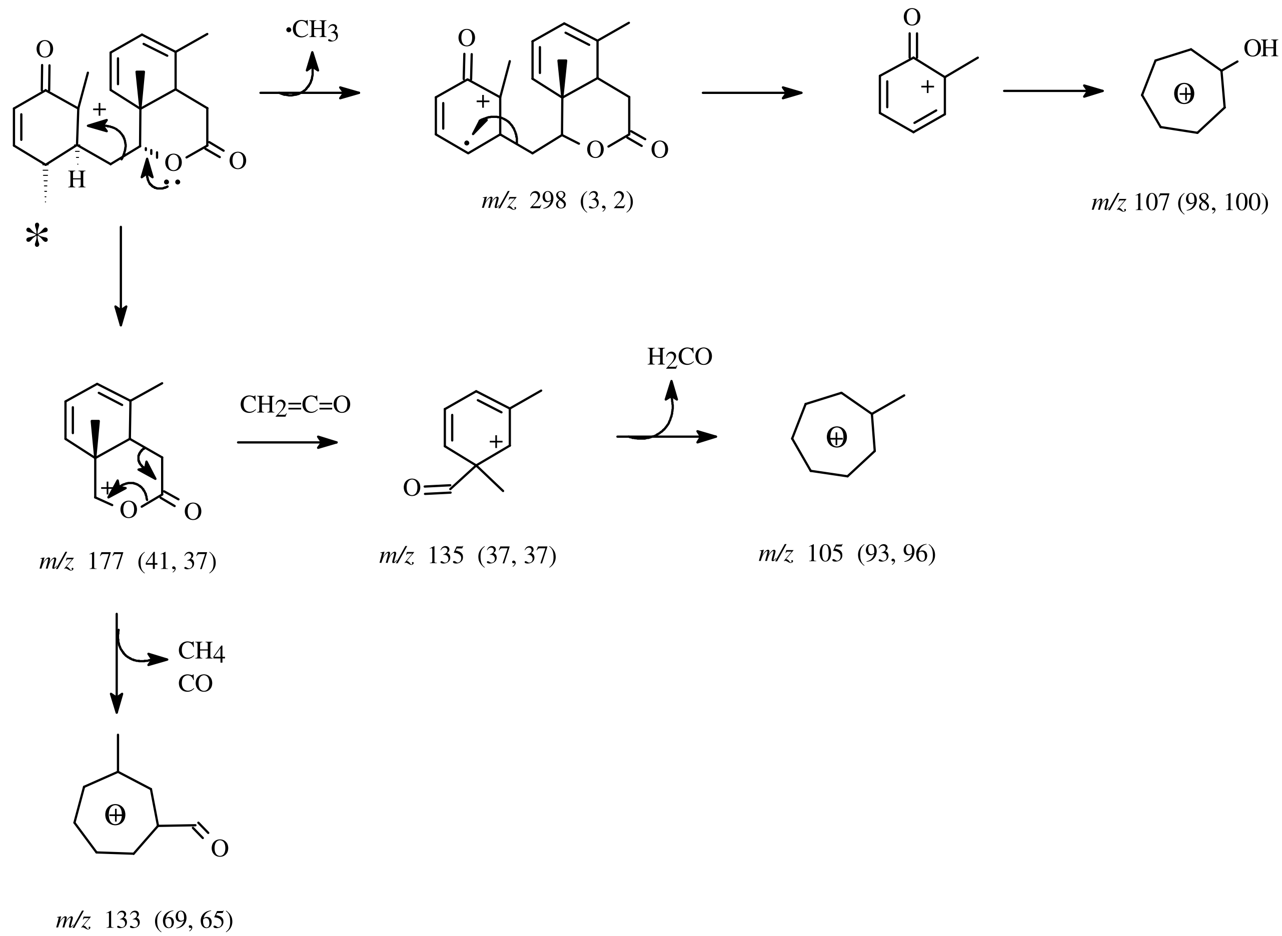
Table 4. ^1H x ^1H-NOESY data (400 MHz) of **2a** and **2b***.

	2a			**2b**		
H	δ_H	H	δ_H	δ_H	H	δ_H
2ax	5.56	3eq	2.32	5.56	3eq	2.33
		4ax	2.05		4ax	2.04
		19	1.24		19	1.24
11ax	4.94	21b	4.30	4.92	20	4.30
		-	-		22	2.75
		12eq	2.49		12eq	2.49
		19	1.24		19	1.24
		30	0.90		30	0.89
21[a]	4.59	20	4.31	4.60	21b	4.34
		21b	4.30		20	4.30
20	4.31	14	2.63	4.30	14	2.63
					12eq	2.49
					18	0.98
21b	4.30	12eq	2.49	4.34	30	0.89
		18	0.98			
		30	0.90			
7	4.18	14	2.63	4.17	14	2.63
		6eq	1.96		6eq	1.96
		6ax	1.76		6ax	1.75
		30	0.90		30	0.89
9	2.78	12ax	1.69	2.78	12ax	1.69
		5	1.47		5	1.48
14	2.63	18	0.98	2.63	18	0.98
		30	0.90		30	0.89
22	2.75	-	-	2.75	30	0.89
6ax	1.76	30	0.90	1.75	30	0.89
		4	2.05		4	2.04

* The unequivocal assignment of the hydrogen atoms δ_H were based on the HMBC spectra of **2a** and **2b**.



Scheme 1. Suggested EIMS fragmentation pathways for **2a** and **2b** (%: respectively **2a** and **2b**).



Scheme 1. Suggested EIMS fragmentation pathways for **2a** and **2b** (continuation).

300 model, equipped with 300 columns (42.0 x 0.3 cm) and also with Merck silica gel columns (40-60 µm) were used.

Plant material

The aerial parts of *Simaba cuneata* St.Hill. were collected in January of 1993, in highway of Sol, Guarapari - ES, and were identified by Prof. Dr. José Rubens Pirani. The respective voucher can be found deposited in the Herbarium of the São Paulo University, Biosciences Institute - SP. The leaves, bark and branches were dried separately in a stove with a circulation of air at 30 °C and afterwards were milled in a Willey mill.

Extraction and isolation of the chemical constituents

The branches (680 g) were extracted consecutively with hexane and methanol at room temperature. After distillation of the solvents were obtained, respectively, 2.1 g and 6.4 g of solid residues. The residue obtained from the MeOH extraction (~5.5 g) was submitted to droplet countercurrent chromatography in descendent mode, using $CHCl_3$:MeOH:H_2O (5:5:3 v/v) as solvent. The organic phase was mobile and the aqueous phase was stationary. After 56 h of analysis, 259 fractions, 13 mL each, were collected and divided into 8 groups based on the results from analytical TLC. The fraction 3 (789 mg) was submitted to chromatography on a silica gel column, under pressure, using $CHCl_3$:MeOH (95:5 initial v/v) as eluent, with an eluting gradient till MeOH (100%). 20 fractions, 20 mL each, were obtained. The fractions 3 (420 mg) and 4 (120 mg) have supplied, respectively, the impure quassinoids **1a** and **1b**.

Acetylated derivations

The fractions 3 (420 mg) and 4 (120 mg), previously described, were acetylated with acetic anhydride/pyridine (2:1), as usual, during 12 h. The acetylated derivatives **2a** (395 mg) and **2b** (8 mg) were obtained and purified by re-crystallization in MeOH.

20(R)-2-O-acetylsimarolide (**2a**). m.p. > 280 °C. $[\alpha]_D$ = -14.0° (c 0.8, $CHCl_3$). ^{13}C-NMR (100 MHz): Table 1 and ^1H-NMR (400 MHz): Table 2. MS *m/z* (relative intensity, %): $M^{+\bullet}$ 546 (1.4 %), 486 (37), 427 (7), 426 (20), 373 (21), 177 (41), 135 (37), 133 (69), 119 (100), 113 (70), 107 (98), 105 (93).

20(S)-2-O-acetylsimarolide (**2b**). m.p. > 280 °C. $[\alpha]_D$ = -19.2° (c 1.48, $CHCl_3$). ^{13}C-NMR (100 MHz): Table 1 and ^{1}H-NMR (400 MHz): Table 2. MS, *m/z* (relative intensity, %): 546 (1 %), 486 (29), 427 (5), 426 (16), 373 (16), 177 (37), 135 (37), 133 (65), 119 (99), 113 (67), 107 (100), 105 (96).

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