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Short Report

New Spectral Data of Some Flavonoids from *Deguelia hatschbachii* A.M.G. Azevedo

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Entre os flavonóides isolados de *Deguelia hatschbachii*[1] encontram-se escandenina (**1**), robustato de metila (**2**) e *4',5-diidroxi-6-(3,3-dimetilalila)-7-metoxiflavanona* (**3**) que foram identificados pela comparação dos dados espectroscópicos previamente publicados. A obtenção de novos dados espectroscópicos (RMN, RMN-2D e EM/EM) permitiu a atribuição dos deslocamentos químicos de todos os hidrogênios e carbonos nos espectros de RMN ^{1}H e ^{13}C destas substâncias, assim como a elucidação dos caminhos de fragmentação de **1**-**3** no espectrômetro de massas.

From the roots of *Deguelia hatschbachii,* the known flavonoids scandenin (**1**), methyl robustate (**2**) and *4',5- dihydroxy-6-(3,3-dimethylalyll)-7-methoxy flavanone* (**3**) were isolated and characterized by comparison of their spectroscopic data with those found in the literature. Now the inclusion of 1D- and 2D-NMR and MS/MS data has allowed the complete assignment of all hydrogen and carbon chemical shifts in their NMR spectra, as well as the elucidation of the fragmentation pathways of **1**-**3** in the mass spectrometer.

Keywords: *Deguelia hatschbachii*, Leguminosae, 4-hydroxy-3-phenylcoumarins, flavanone

Introduction

Deguelia hatschbachii A. M. G. Azevedo (Leguminosae-Fabaceae) is a new species native to Brazil. It is a medium sized tree, 3-6 m in height, with pink flowers and can be found in the East-south of Minas Gerais State and in the region of Mata Atlântica along the states of Espírito Santo, Rio de Janeiro and São Paulo.

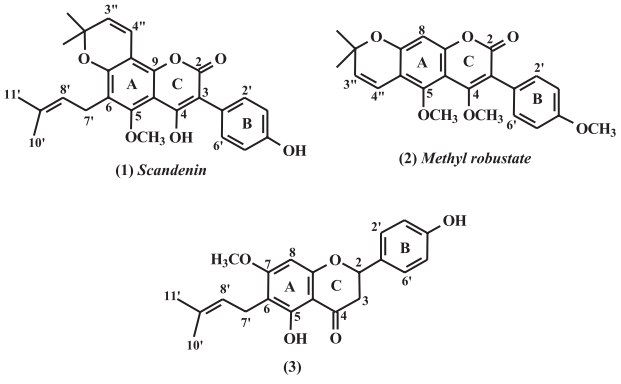

Figure 1. Compounds isolated from *Deguelia hatschbachii*.

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In a previous report[1] we described the structural determination of five new compounds, which were isolated together with eight known ones from the roots of *D. hatschbachii*.

Since the ^{1}H and ^{13}C NMR literature data for compounds **1-3** are incomplete (Figure 1), in this paper we report the complete assignment of ^{1}H and ^{13}C NMR spectral data of **1-3** by using 1D- and 2D- NMR techniques as well as the fragmentation pathways of **1** and **3** in the mass spectrometer, based on MS/MS experiments.

Experimental

General experimental procedures

^{1}H NMR (300 and 500 MHz), ^{13}C NMR (75 MHz), ^{1}H-^{13}C HETCOR J^{1}_{CH} and ^{1}H-^{13}C COLOC J^{n}_{CH} (n=2 and 3) spectra were recorded using BRUKER AC 300/P, GEMINI 2000 (VARIAN), GEMINI 300 BB (VARIAN) and INOVA 500 (VARIAN) spectrometers, with TMS as internal standard and $CDCl_3$ as solvent. Chemical shifts (δ) are in ppm and the coupling constants (J) in Hertz (Hz).

EIMS 70 eV, direct probe, MS/MS experiments were performed in a VG Auto Spec-Fisions Instrument by using

electron ionization technique at 70 eV (linked scan at 8KeV collisions with Helium).

Plant material, extraction and isolation[1]

4,4'-dihydroxy-3-phenyl-5-methoxy-6-(3,3-dimethylallyl)-2",2"-dimethylchromene (5",6":8,7)-coumarin (**1**, *Scandenin*). ^{1}H NMR spectral data (300 MHz, $CDCl_3$/TMS): Table 1. ^{13}C NMR spectral data (75 MHz, $CDCl_3$): Table 2. EIMS (probe) 70 eV, *m/z* (rel. int.): 434 $[M]^+$ (100), 419 $[M\text{-}Me]^+$ (70), 391 $[M\text{-}Me\text{-}CO]^+$ (4), 379 $[M\text{-}55]^+$ (3), 363 $[M\text{-}Me\text{-}56]^+$ (3), 300 $[M\text{-}134]^+$ (7), 285 $[M\text{-}134\text{-}Me]^+$ (66), 245 $[M\text{-}189]^+$ (12), 257 $[M\text{-}134\text{-}Me\text{-}CO]^+$ (12).

4, 5, 4'-trimethoxy-3-phenyl-2", 2"-dimethylchromene (5", 6": 6,7) coumarin (**2**, *Methyl robustate*). ^{1}H NMR spectral data (300 MHz, $CDCl_3$/TMS): Table 1. ^{13}C NMR spectral data (75 MHz, $CDCl_3$): Table 2. EIMS (probe) 70 eV, *m/z* (rel. int.): 394 $[M]^+$ (33), 379 $[M\text{-}Me]^+$ (100), 366 $[M\text{-}CO]^+$ (1), 351 $[M\text{-}CO\text{-}Me]^+$ (2), 135 $[M\text{-}CO\text{-}Me\text{-}216]^+$ (12).

5, 4'-dihydroxy-6-(3,3-dimethylallyl)-7-methoxy-flavanone (**3**). ^{1}H NMR spectral data (500 MHz, $CDCl_3$/TMS): Table 1. ^{13}C NMR spectral data (75 MHz, $CDCl_3$): Table 2. EIMS (probe) 70 eV, *m/z* (rel. int.): 354 $[M]^+$ (100), 339 $[M\text{-}Me]^+$ (29), 311 $[M\text{-}Me\text{-}CO]^+$ (28), 299 $[M\text{-}55]^+$ (27), 234 $[M\text{-}120]^+$ (11), 219 $[M\text{-}120\text{-}Me]^+$ (43), 206 $[M\text{-}120\text{-}CO]^+$ (20), 191 $[M\text{-}120\text{-}CO\text{-}Me]^+$ (17), 179 [M-175] (56), 120 $[M\text{-}234]^+$ (18), 119 $[(M+H)\text{-}234]^+$ (8), 91 $[(M+H)\text{-}234\text{-}CO]^+$ (13).

Results and Discussion

Scandenin **1** was previously isolated from *Derris spruceana*[2] and *Derris scandens*.[3] We now report, for the first time, its ^{13}C NMR spectral data (Table 2). The carbon resonances were identified by extensive 2D- NMR correlation experiments [HETCOR and COLOC] (Table 3).

Based on MS/MS experiments selecting the ions of *m/z* 419 [391 (6%), 285 (100%)], *m/z* 300 [285 (100%), 269 (22%), 257 (48%), 245 (65%), 229 (17%)] e *m/z* 134 [106 (100%)] we can confirm the fragmentation pathway[4] for this compound (Figure 2).

Methyl robustate **2** was previously isolated from *Derris robusta*[5] when only UV, IR and low resolution ^{1}H NMR (60 MHz) spectral data were reported. We now include ^{1}H (300 MHz), ^{13}C NMR data (Tables 1 and 2) and the fragmentation pathway for this compound (Figure 3).

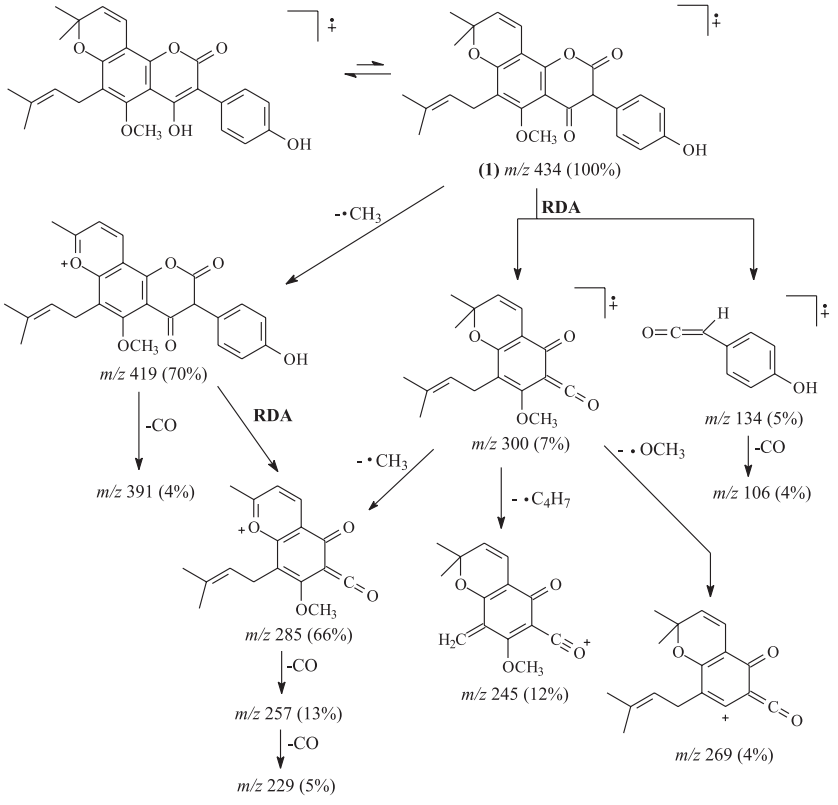

Figure 2. Fragmentation pathway of scandenin **1**, based on MS/MS experiment.

Table 1. ^{1}H NMR values of 4-hydroxy-3-phenylcoumarins **1, 2** and flavanone **3**

H	Scandenin 1[a] δ	Methyl robustate 2[a] δ	Flavanone 3[b] δ
2"-2CH_3	1.47 (6H, s)	1.47 (6H, s)	-
11'	1.71 (3H, s)	-	1.69 (3H, s)
10'	1.79 (3H, s)	-	1.78 (3H, s)
3 *eq*	-		2.76 (1H, dd, *J* 17.1 and 2.2)
3 *ax*	-	-	3.08 (1H, dd, *J* 17.1 and 13.4)
7'	3.33 (2H, d, *J* 6.7)	-	3.27 (2H, d, *J* 6.3)
4-OCH_3	-	3.56 (3H, s)	-
5-OCH_3	3.93 (3H, s)	3.82 (3H, s)	-
7-OCH_3		-	3.82 (3H, s)
2	-	-	5.30 (1H, dd, *J* 13.4 and 2.2)
8	-	6.62 (1H, d, *J* 0.7)	6.07 (1H, s)
4'-OCH_3	-	3.85 (3H, s)	-
8'	5.17 (1H, m)	-	5.20 (1H, tl, *J* 6.3)
OH-4'	5.17 (1H, sl)	-	-
3"	5.69 (1H, d, *J* 10.0)	5.71 (1H, d, *J* 10.2)	-
4"	6.90 (1H, d, *J* 10.0)	6.65 (1H, dd, *J* 10.2 and 0.7)	-
3' and 5'	6.89 (2H, d, *J* 8.6)	6.97 (2H, d, *J* 8.9)	6.88 (2H, d, *J* 8.2)
2' and 6'	7.42 (2H, d, *J* 8.6)	7.41 (2H, d, *J* 8.9)	7.29 (2H, d, *J* 8.2)
OH-4	10.21 (1H, s)	-	-
OH-5	-	-	12.03 (1H, s)

[a] ^{1}H NMR values (300 MHz); [b] ^{1}H NMR values (500 MHz).

Table 2. ^{13}C NMR values (75 MHz, $CDCl_3$) of 4-hydroxy-3-phenylcoumarins **1**, **2** and flavanone **3**

C	1	2	3
2	160.8	163.1	79.1
3	103.5	105.3	43.3
4	162.9	164.4	196.1
5	153.9	152.8	160.2
6	106.7	112.9	110.0
7	155.2	159.3	165.5
8	119.1	101.1	91.0
9	147.2	154.8	161.4
10	101.3	112.8	102.9
1'	123.2	124.0	130.6
2'	131.8	131.8	127.9
3'	115.2	113.7	115.6
4'	155.2	157.0	156.1
5'	115.2	113.7	115.6
6'	131.8	131.8	127.9
7'	22.4	-	21.0
8'	121.7	-	122.2
9'	132.5	-	131.7
10'	18.0	-	17.7
11'	25.7	-	25.8
2"	78.1	77.5	-
3"	115.3	115.9	-
4"	129.6	130.6	-
$2CH_3$-2"	28.1	28.2	-
5-OCH_3	63.9	63.4	-
4'-OCH_3	-	55.3	-
4-OCH_3	-	61.3	-
7-OCH_3	-	-	55.8

Table 3. Observed correlation in HETCOR (vicinal C-H) and in COLOC (long-range C-H) spectra ($CDCl_3$, 7 Tesla) of **1**

H (δ)	C (δ,J^1)	C (δ,J^n)
HO-4 (10.21)	-	3 (103.5)
2' (7.42)	2' (131.8)	4'(155.2)
3' (6.89)	3' (115.2)	1'(123.2)
5' (6.89)	5' (115.2)	1'(123.2)
6' (7.42)	6' (131.8)	4'(155.2)
4" (6.90)	4" (129.6)	-
3" (5.69)	3" (115.3)	-
7' (3.33)	7' (22.4)	7 (155.2); 5 (153.9); 8'(121.7); 8 (119.1)
8' (5.17)	8' (121.7)	-
$\underline{H}_3CO$-5 (3.93)	$H_3\underline{C}O$-5 (63.9)	5 (153.9)
10' (1.79)	10' (18.0)	9'(132.5); 8'(121.7); 11'(25.7)
11' (1.71)	11' (25.7)	9'(132.5); 8'(121.7); 10'(18.0)
2"-2$C\underline{H}_3$ (1.47)	2"-2$\underline{C}H_3$ (28.1)	2" (78.1); 4"(129.6)

The ^{1}H NMR spectrum of compound **3** showed the same absorptions found for the flavanone previously isolated from *Lonchocarpus minimiflorus*,[6] when only MS and low resolution ^{1}H NMR (90 MHz) spectral data were reported. 1D- and 2D- NMR experiments allowed the full assignment of all hydrogen and carbon shift values (Tables 1, 2, 4 and 5).

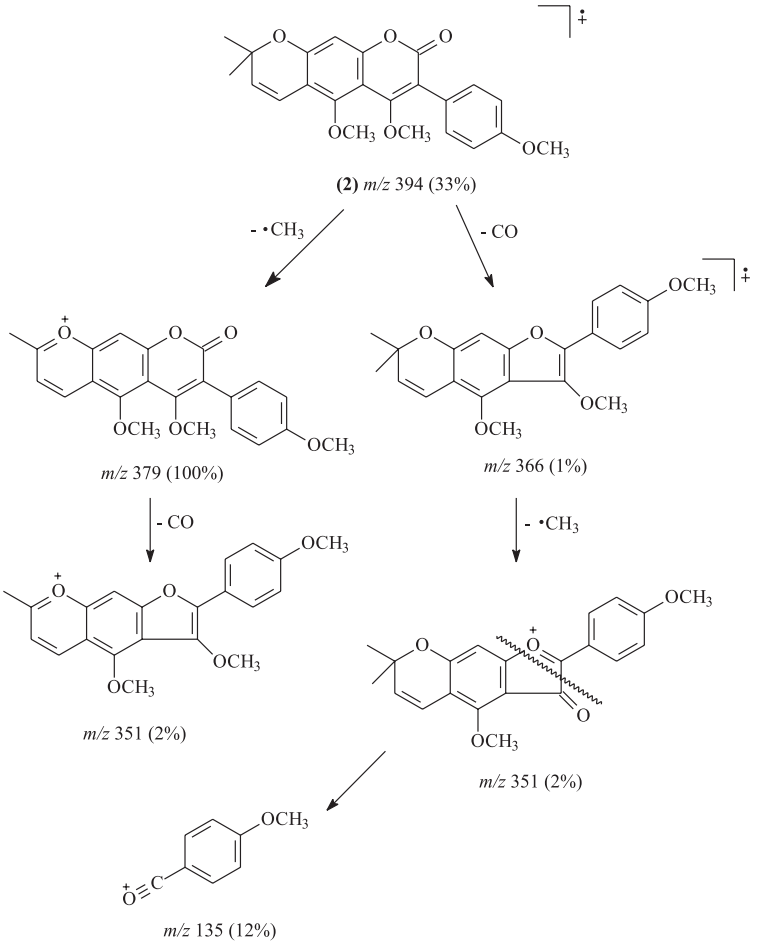

Figure 3. Fragmentation pathway of methyl robustate **2**.

Table 4. Observed correlation in COSY (H-H) spectra ($CDCl_3$, 7 tesla) of **3**

H (δ)	H (δ, J^n)
2' and 6' (7.29)	3' and 5' (6.88)
2 (5.30)	3*ax* (3.08) and 3*eq* (2.76)
8' (5.20)	7' (3.27)
3*ax* (3.08)	3*eq* (2.76)
7' (3.27)	10' (1.78); 11' (1.69)

Based on MS/MS experiments selecting the ions of *m/z* 339 [219 (26%)], *m/z* 206 [191 (27%)] and *m/z* 234 [219 (41%), 206 (11%), 191 (5%), 179 (24%)] we can suggest a fragmentation pathway for this compound (Figure 4).

Conclusions

The combination of 1D- and 2D-NMR techniques has allowed the complete assignment of the ^1H and ^{13}C spectral

Table 5. Observed correlation in HETCOR (vicinal C-H) and in COLOC (long-range C-H) spectra ($CDCl_3$, 7 Tesla) of **3**

H (δ)	C (δ, J^1)	C (δ, J^n)
HO-5 (12.03)	-	5 (160.2); 6 (110.0)
2 (5.30)	2 (79.1)	-
3 (3.08)	3 (43.3)	2(79.1); 4 (196.1)
3 (2.76)	3 (43.3)	4 (196.1)
8 (6.07)	8 (91.0)	10 (102.9); 9 (161.4)
2' (7.29)	2' (127.9)	4'(156.1)
3' (6.88)	3' (115.6)	1'(130.6)
5' (6.88)	5' (115.6)	1'(130.6)
6' (7.29)	6' (127.9)	4'(156.1)
7' (3.27)	7' (21.0)	5 (160.2); 6 (110.0)
8' (5.20)	8' (122.2)	-
H_3CO-7 (3.82)	H_3CO-7 (55.8)	7 (165.5)
10' (1.78)	10' (17.7)	8'(122.2); 9'(131.7)
11' (1.69)	11' (25.8)	8'(122.2); 9'(131.7)

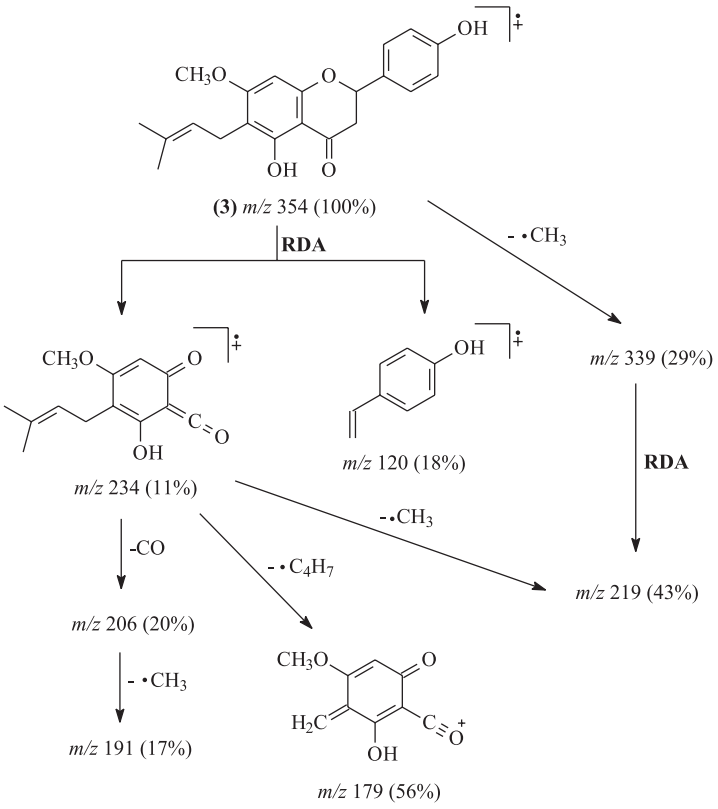

Figure 4. Fragmentation pathway of flavanone **3**, based on MS/MS experiment.

data of the known flavonoids **1-3,** until now not found in the literature.

Our results will fill the gap in literature data for these compounds, which are rarely found in nature and can be used to facilitate further assignments of other analogous flavonoids.

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References

1. Magalhães, A. F.; Tozzi, A. M. G. A.; Magalhães, E. G.; Moraes, V. R. D.; *Phytochemistry* **2001**, *57*, 77.
2. Garcia, M.; Kano, M. H. C.; Vieira, D. M.; do Nascimento, M. C.; Mors, W. B.; *Phytochemistry* **1986**, *25*, 2425.
3. Clark, E.P.; *J. Org. Chem.* **1943**, *8*, 489.
4. Pelter, A.; Stainton, P.; Johnson, A. P.; Barber, M.; *J. Heterocycl. Chem. 2* **1965**, 256.
5. Johnson, A.P.; Pelter, A.; *J. Chem. Soc. (C)* **1966**, 606.
6. Mahmoud, E. N.; Waterman, P. G.; *J. Nat. Prod.* **1985**, *48*, 648.

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