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Short Report

New Isoflavone Derivative and Other Flavonoids from the Resin of *Amburana cearensis*

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A investigação fitoquímica da resina de *Amburana cearensis* A. C. Smith permitiu o isolamento de um novo composto: 3',4'-dimetóxi-1'-(7-metóxi-4-oxo-4H-cromen-3-il) benzo-2',5'-quinona (**1**), juntamente com seis compostos conhecidos e identificados como: 4,2',4'-triidroxichalcona (**2**), 7,8,3',4'-tetrametoxiisoflavona (**3**), 4,2',4'-triidroxi-3-metoxichalcona (**4**), 3,4,5-trimetoxicinamaldeido (**5**), 3',4'-dimetoxi-7-hidroxiisoflavona (**6**) e 6,7,4'-trimetoxi-3'-hidroxiisoflavona (**7**). As estruturas foram estabelecidas com base na análise dos dados espectrométricos de: IV, EI-EM, HR-ESI-EM e RMN incluindo experimentos 2D.

Phytochemical investigation of the resin of *Amburana cearensis* A. C. Smith allowed the isolation of a new compound: 3',4'-dimethoxy-1'-(7-methoxy-4-oxo-4H-cromen-3-yl)benzo-2',5'-quinone (**1**), together with six known compounds identified as: 4,2',4'-trihydroxychalcone (**2**), 7,8,3',4'-tetramethoxyisoflavone (**3**), 4,2',4'-trihydroxy-3-methoxychalcone (**4**), 3,4,5-trimethoxycinnamaldehyde (**5**), 3',4'-dimethoxy-7-hydroxyisoflavone (**6**) and 6,7,4'-trimethoxy-3'-hydroxyisoflavone (**7**). The structures were established from the IR, HR-ESI-MS and NMR spectral data, including 2D-NMR experiments.

Keywords: *Amburana cearensis*, resin, phytochemical investigation, flavonoids

Introduction

Amburana cearensis A. C. Smith (Sin. *Torrensea cearensis* Fr. AlI), Leguminoseae family, Papilionoideae (Fabaceae), is a tree popularly known as "imburana de cheiro", "cerejera" and "cumaru" in northeast of Brazi1.[1,2] The syrup of trunk bark is used in folk medicine for treatment of respiratory diseases as cold, bronchits and asthma. Pharmacological studies using hydroalcoolic syrup from the bark trunk showed anti-inflammatory, analgesic, bronchodilator and antinociceptive activities.[3-6] Recent studies[7] have shown that amburoside A, isokaempferide, kaempferol and polyphenols isolated from the trunk bark of *A. cearensis* also showed present neuroprotective, antioxidant, antiinflamatory, anticarcinogenic and hepatoprotective activities.

Previous studies with the bark from *A. cearensis* resulted in the isolation of 4-(O-β-D-glucopyranosyl)-hydroxy-7-(3',4'-dihydroxy-benzoyl)-benzyl, 4-(*O*-β-*D*-glucopyranosyl)-hydroxy-7-(3'-methoxy-4'-hydroxy-benzoyl)-benzyl, coumarin, sucrose, vanilic acid, protocatechuic acids, afrormosin, isokaempferide, kaempferol, quercetin, 4' -methoxy-fisetin, amburoside A and a mixture of β-sitosterol and stigmasterol glucoside).[8,9] Phytochemical investigation was carried out recently with especies obtained from seed germinations.[10]

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This paper describes the chemical investigation of the resin of *A. cearensis*, which resulted in the isolation of a new compound named as 3’,4’-dimethoxy-l’-(7-methoxy-4-oxo-4H-cromen-3-yl)benzo-2’,5’-quinone (**1**).

Experimental

General procedure

The melting point was determined using a Mettler Toledo FP82HT micromelting point apparatus. The IR spectra were measured in KBr pellets, using Perkin-Elmer, FT-IR Spectrum 1000. All the NMR data were recorded using a Bruker Avance DPX 300 and Avance DRX-500 spectrometer operating in the frequency of the hydrogen at 300.13 and 500.13 MHz in the frequency of the carbon for 75.47 and 125.75 MHz. The spectra were recorded in CDCl$_{3,}$ C$_5$D$_5$N and CD$_3$OD. High resolution data were obtained in a MS-IT-TOF mass spectrometer.

Plant material

The resin of *A. cearensis* was collected in city of Limoeiro do Norte, Ceará, Brazil. The plant material was identified in the Departamento de Biologia do Centro de Ciências da Universidade Federal do Ceará, Brazil. A voucher (No. 847) specimen is deposited in the Herbarium Prisco Bezzera of this University.

Extraction and isolation

The resin (400 g) was submitted to an extraction with EtOH at room temperature and yielded (23.46 g). The EtOH extract was dissolved in 200 mL of water and partitioned in the CHCl$_3$ and EtOAc yielded (8.1 g) and (0.7 g) respectively. The EtOAc fraction (0.7 g) was subjected to CC on SiO$_2$ using EtOAc, CHCl$_3$ and MeOH. The CHCl$_3$ fraction (0.15 g) was chromatographed in sephadex LH-20 column using MeOH, obtaining compound **1** (18 mg) and **2** (30 mg). The CHCl$_3$ fraction (8.1 g) was subjected to CC on SiO$_2$ using EtOAc, CHCl$_3$ and MeOH. The CHCl$_3$ fraction (0.30 g) was successively chromatographed in sephadex LH-20 column using MeOH and obtaining compound **3** (40 mg), **4** (23 mg), **5** (15 mg), **6** (10 mg) and **7** (16 mg).

3’,4’-Dimethoxy-1’-(7-methoxy-4-oxo-4H-cromen-3-yl) benzo-2’,5’-quinone (1)

Orange solid, mp 196-198 °C; IR (KBr) ν_{max}/cm^{-1}: 1649, 1628, 1595, 1439, 1279, 1100, 835; ^{1}H and ^{13}C NMR (see Table 1); HR-ESI-MS spectrum revealed formation of molecular ions *m/z* 343.0931 ($C_{18}H_{14}O_7$ + H$^+$), 365.0661

Table 1. ^{1}H NMR (500 MHz) and ^{13}C NMR (125 MHz) data of **1** (in CDCl$_3$) compared with values of **8** (DMSO-d_6, (dd, ppm), *J* in Hz*

	1				**8**	
	^{1}H,^{13}C-HMQC		^{1}H,^{13}C-HMBC			
	δ (C)	*δ* (H)	^2J	^3J	*δ* (C)	*δ* (H)
C(2)	156.5	8.16 (s)			157,5	8.36 (s)
C(3)	116.3		H-2	H-6’	115.5	
C(4)	174.4			H-2; H-5	178.8	
C(5)	127.9	8.15 (d, *J* 8.9)			161.6	
C(6)	115.1	7.02 (dd, *J* 8.9, 2.3)		H-8	99.5	6.44 (d, *J* 1.5)
C(7)	165.0		H-6; H-8	MeO-7	164.7	
C(8)	100.4	6.88 (d, *J* (2.3)		H-6	94.1	6.27 (d, *J* 1.5)
C(9)	158.0		H-8	H-2	157.1	
C(10)	118.0			H-6; H-8	104.0	
C(1’)	135.0		H-6’	H-2	137.9	
C(2’)	183.9			H-6’; MeO-2’	185.0	
C(3’)	145.0			MeO-3’	107.9	6.26 (s)
C(4’)	158.2			MeO-4’; H-6’	158.4	
C(5’)	183.9				181.4	
C(6’)	133.9	7.17(s)			133.2	7.05 (s)
MeO-7	55.9	3.93 (s)				
MeO-3’	61.2	4.03 (s)				
MeO-4’	61.5	4.08 (s)			56.3	3.83 (s)

*Number of hydrogens bound to carbon atoms deduced by comparative analysis of ^{1}H and DEPT ^{13}C NMR spectra. Chemical shifts and coupling constants (*J*) were obtained of 1D ^{1}H NMR spectrum. ^{1}H,^{1}H COSY and ^{1}H, ^{1}H NOESY experiments were also used for these assignments in compared with literature data **8** (ref. 13).

($C_{18}H_{14}O_7$ + Na$^+$) and 381.0438 ($C_{18}H_{14}O_7$ + K$^+$). LR-EI-MS *m/z* (rel; Int.): ([M$^+$], 94.5%), 200 [M$^+$ – 142] 100%, 150 [M$^+$ – 193] 32.9%, 327 [M$^+$ – 15] 8.2%.

Results and Discussion

Compound **1** was obtained as orange solid. The HR-ESI-MS spectrum showed a pseudo molecular íons peaks at *m/z* 343.0931 ($C_{18}H_{14}O_7$ + H$^+$, requires 343.0818), 365.0661 ($C_{18}H_{14}O_7$ + Na$^+$, requires 365.0637) and 381.0438 ($C_{18}H_{14}O_7$ + K$^+$, requires 381.0377). The IR spectrum exhibited bands at 1650, 1628 and 1595 ($\nu_{c=0}$) cm^{-1} suggesting the presence of three conjugated carbonyl groups.[11,12] Comparative analysis of the ^{1}H and DEPT ^{13}C NMR spectra (Table 1) allowed to recognize signals for three methoxyl groups and fifteen sp^2 carbons: five methines (including one linked to oxygen atom at δ_c 156.5, compatible with CH-2 of isoflavones) and ten non-hydrogenated [including three carbonyl groups at δ_c 174.4 (C-4), δ_c 183.9 (C-2' and C-5') and four linked to oxygen atoms: δ_c 165.0 (C-7), δc 158.0 (C-9), δc 145.0 (C-3') and δ_c 158.2 (C-4')]. The signals observed in the ^{13}C NMR spectra at δ_c 183.9 and 174.4 were attributed to carbonyl groups at the 1,4-benzoquinone and flavonoid moieties,[13] respectively. Furthermore, the ^{1}H NMR exhibited a characteristic a singlet at δ_H 8.16, assigned to H-2 of an isoflavone, confirmed by HMQC spectrum by the presence of a transversal peak corresponding to direct correlation of this hydrogen signal with ^{13}C signal of methine at δ_c 156.5 (CH-2), and at δ_H 3.93, δ_H 4.03 and δ_H 4.08, corresponding to three methoxyl groups located at C-7, C-3' and C-4', respectively. The location of these methoxyl groups was observed at the heteronuclear long range correlations in the HMBC spectrum (Table 1), which showed correlations of the methoxyl signal at δ_H 3.93 with C-7 (δc 165.0, $^3J_{CH}$, δ_H 4.03 (MeO-3') with δ_c 145.0 (C-3', $^3J_{CH}$) and δ_H 4.08 (MeO-4') with δ_c 158.2 (C-4', $^3J_{CH}$). The presence of a methoxyl group at C-7 was additionally confirmed by nOe effects observed in the ^{1}H, ^{1}H NOESY spectrum, which revealed spatial interactions with the hydrogen atoms H-6 and H-8. The multiplicities of these signals of hydrogen atoms H-6

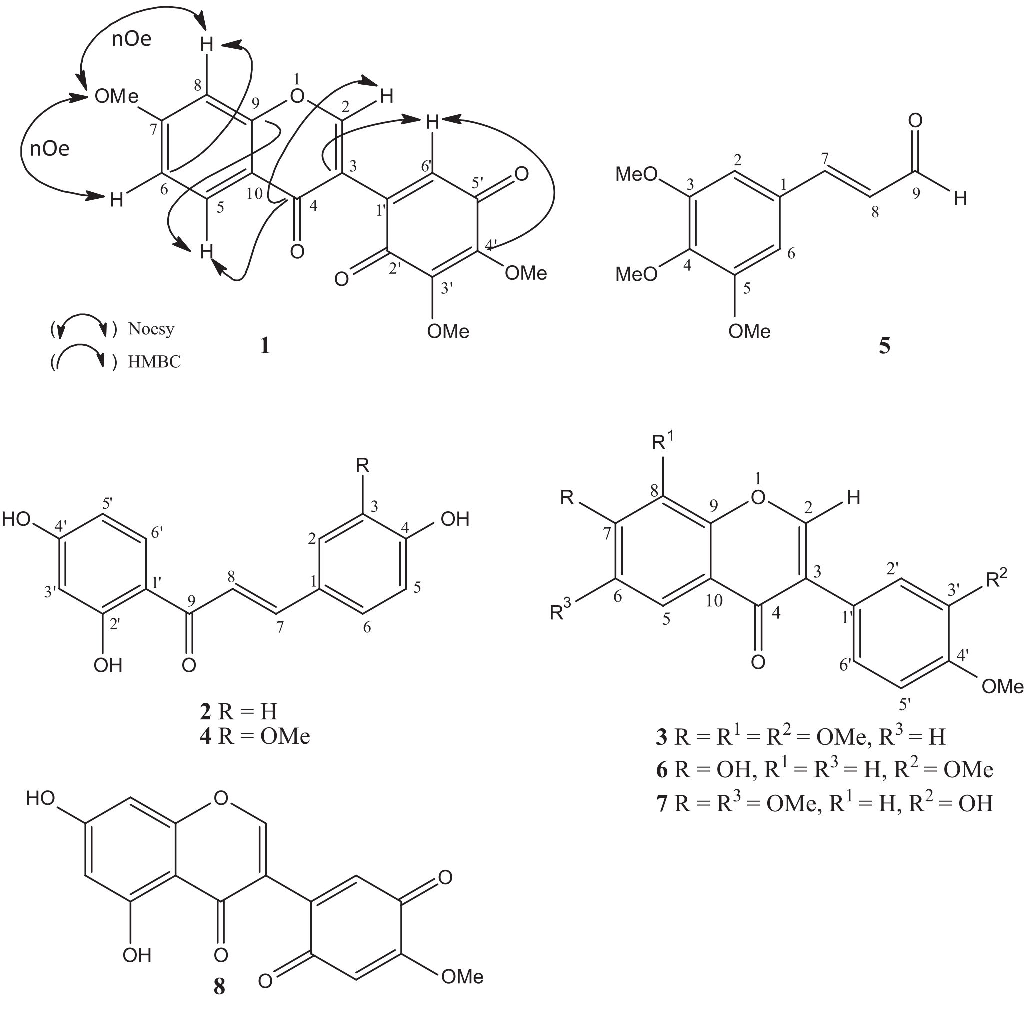

Figure 1. Structure of the chemical constituents (**1-7**) isolated of resin of *Amburana cearensis* A.C Smith and the compound **8** from reference 13.

(δ_H 7.02, dd, J 8.9 and 2.3 Hz) and H-8 (δ_H 6.88, d, J 2.3 Hz) in combination with the corresponding H-5 (δ_H 8.15, d, J 8.9 Hz), correlated via one bond in the HMQC spectrum with the ^{13}C signal at 127.9, allowed to define the ring A, sustaining a methoxyl group at carbon atom C-7. The HMBC spectrum was also used to characterize the presence of a 2,3-dimethoxy-1,4- benzoquinone moiety at C-3 through heteronuclear long range correlation (Table 1) of the carbon C-4’ (δ_c 158.2), with both H-6’ (δ_H 7.17, s, $^3J_{CH}$) and MeO-4’ (δ_H 4.08, s, $^3J_{CH}$), C-3’ (δ_c 145.0) with MeO-3’ (δ_H 4.03, s, $^3J_{CH}$), C-1’ (δ_H 135.0) with both H-2 (δ_H 8.16, s, $^3J_{CH}$) and H-6’ (δ_H 7.17, s, $^2J_{CH}$) and C-3 (δ_c 116.3) with both H-2 (δ_H 8.16, s, $^2J_{CH}$) and H-6’ (δ_H 7.17, s, $^3J_{CH}$). Additional analysis of the ^{13}C NMR spectra of **1** revealed, the ^{13}C chemical shifts (δ_c 145.0) for the C-3’ and (δ_c 158.2) for the C-4’ and for the C-2’/C-5’ (δ_c 183.9), whereby after comparison of these said data with the correspondent values, δ_c 107.9 (CH-3’), δ_c 158.4 (C-4’), δ_c 185.0 (C-2’) and δ_c 181.4 (C-5’), described in the literature,[13] suggests the presence of an additional methoxyl group at carbon C-3’ of **1** as differences observed between spectral data of **1** and of **8** (Table 1). The base peak at *m/z* 200 (100%) observed in the LR-EI-MS, significantly contributed to characterize and to locate the 2,3-dimethoxy-l,4- benzoquinone moiety at C-3 (Figure 1).

Therefore, the structure of compound **1** was assigned as a new isoflavone and it is characterized as 3’,4’-dimethoxy-1’-(7 -methoxy-4-oxo-4H-cromen-3-yl)-benzo-2’,5’-quinone.

The compounds **2**, **3**, **4**, **5**, **6** and **7** were identified through spectroscopic data compared with literature data as: 4,2’,4’-trihydroxychalcone,[14] 7,8,3’,4’-tetrarnethoxy-isoflavone,[15] 4,2’,4’-trihydroxy-3-methoxychalcone,[16] 3,4,5- trimethoxycinnamaldehyde,[17] 3’,4’-dimethoxy-7-hydroxyisoflavone[18] and 6,7,4’-trimethoxy- 3’-hydroxy-isoflavone[19] (Figure 1) , respectively.

Supplementary Information

Supplementary data are available free of charge at http://jbcs.sbq.org.br, as PDF file.

Acknowledgments

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Supplementary Information

New Isoflavone Derivative and others Flavonoids from the Resin of *Amburana cearensis*

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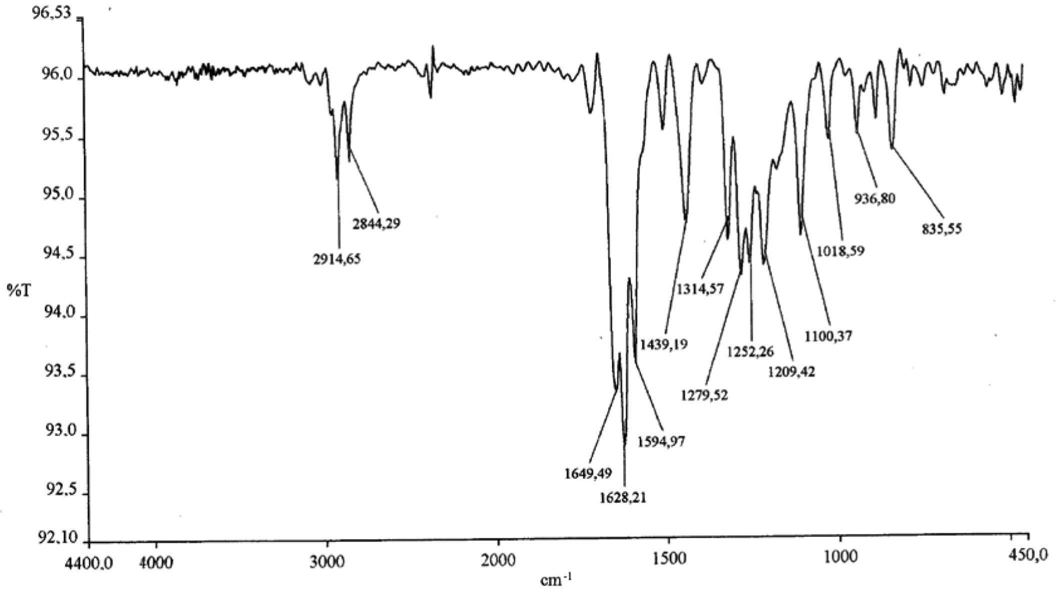

Figure S1. Infrared spectrum of compound **1** (KBr pellets).

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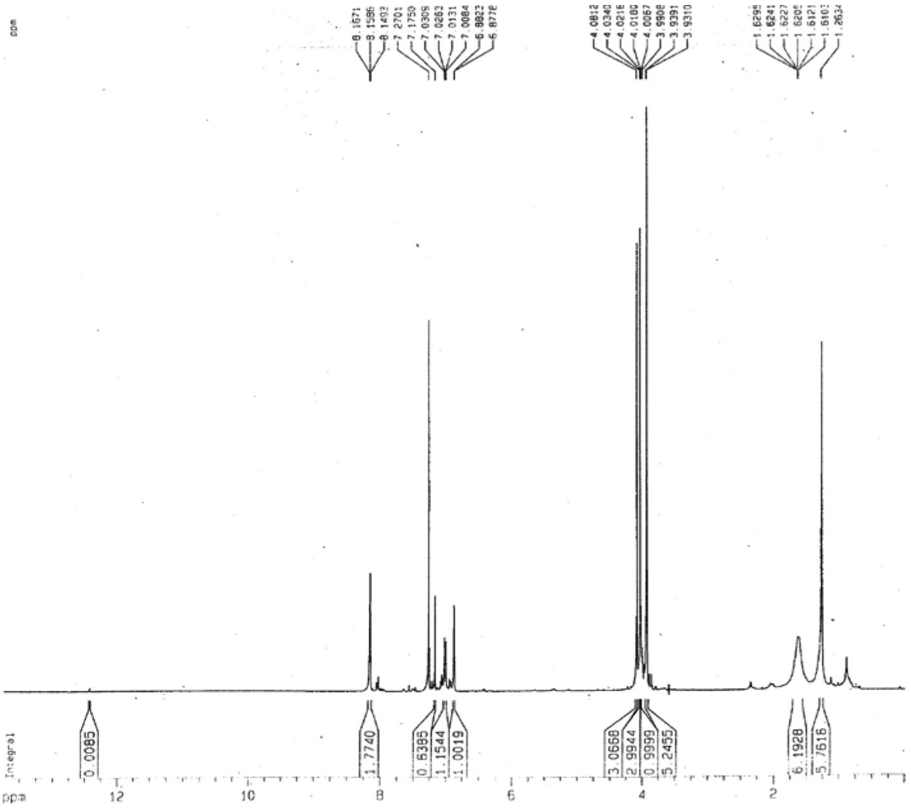

Figure S2. ^{1}H NMR spectrum of **1** (500 MHz, $CDCl_3$).

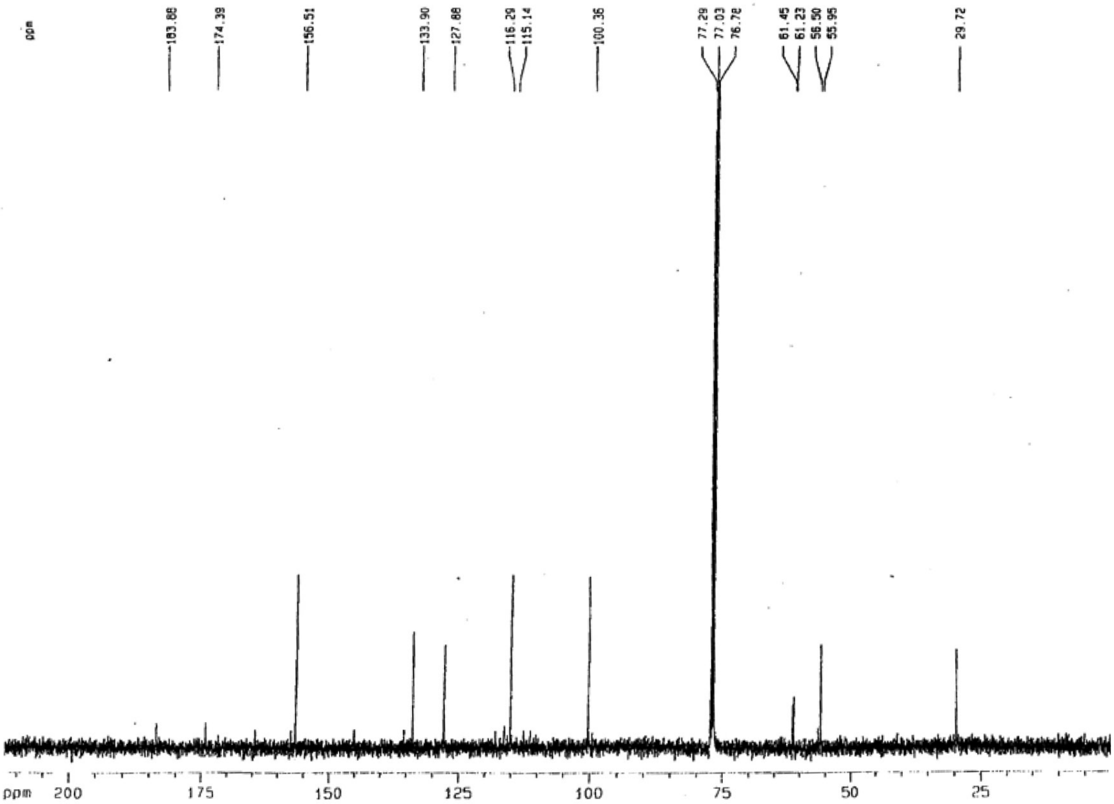

Figure S3. ^{13}C NMR spectrum of **1** (125 MHz, $CDCl_3$).

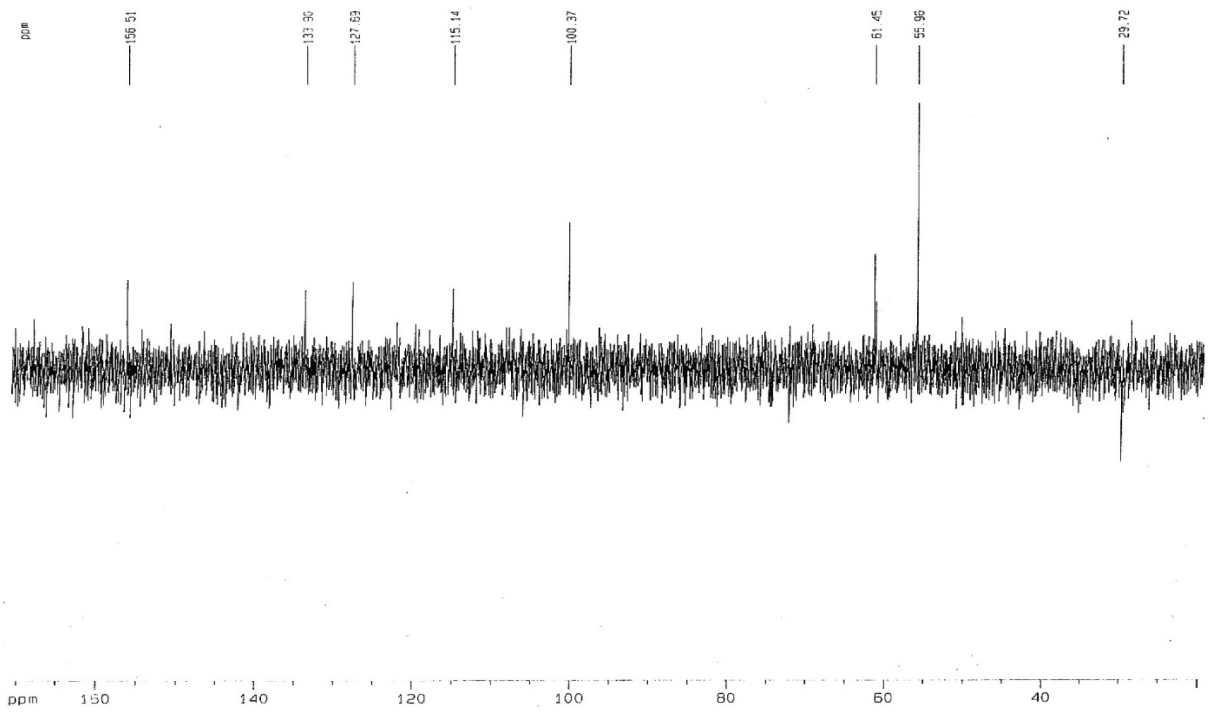

Figure S4. ^{13}C NMR-DEPT 135° of **1**.

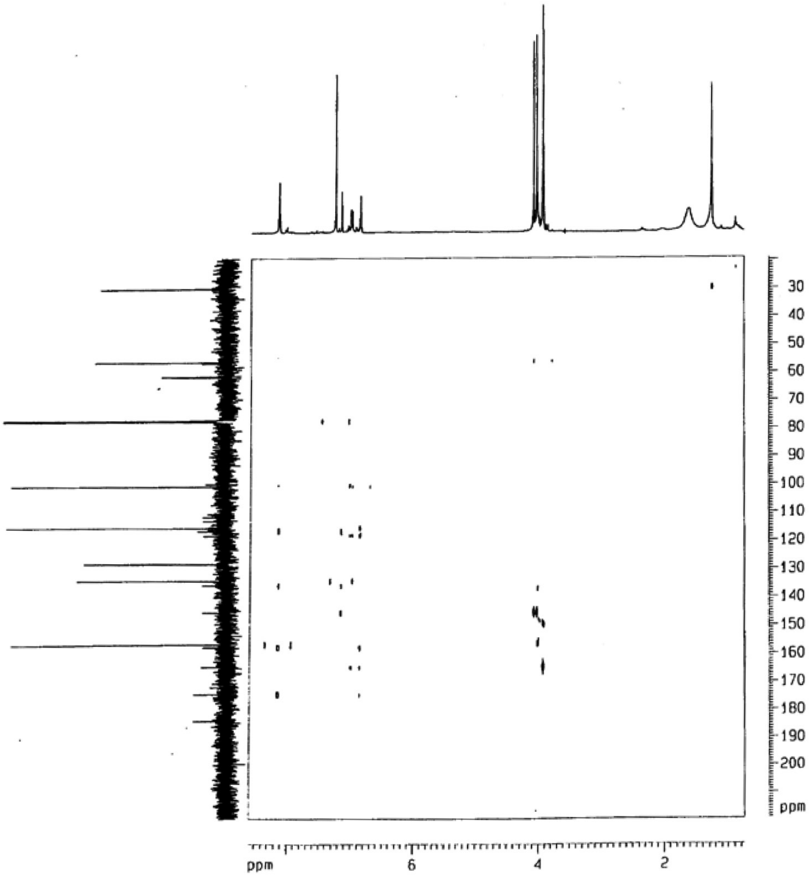

Figure S5. ^{1}H, ^{13}C HMBC-NMR spectrum of **1** (500 MHz, CDCl$_3$).

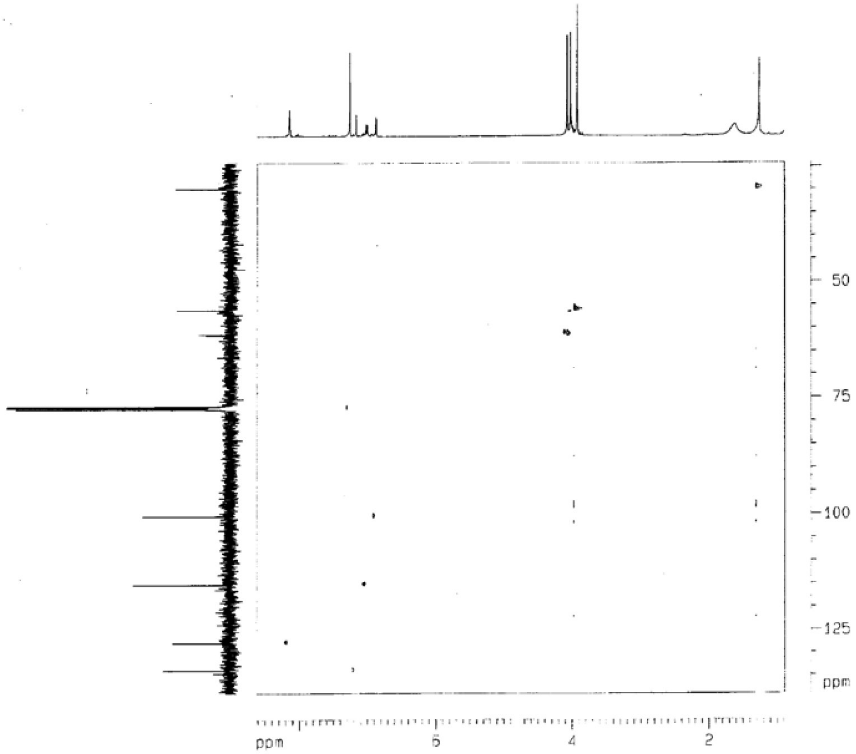

Figure S6. ^{1}H, ^{13}C HMQC-NMR of **1** (500 MHz, CDCl$_3$).

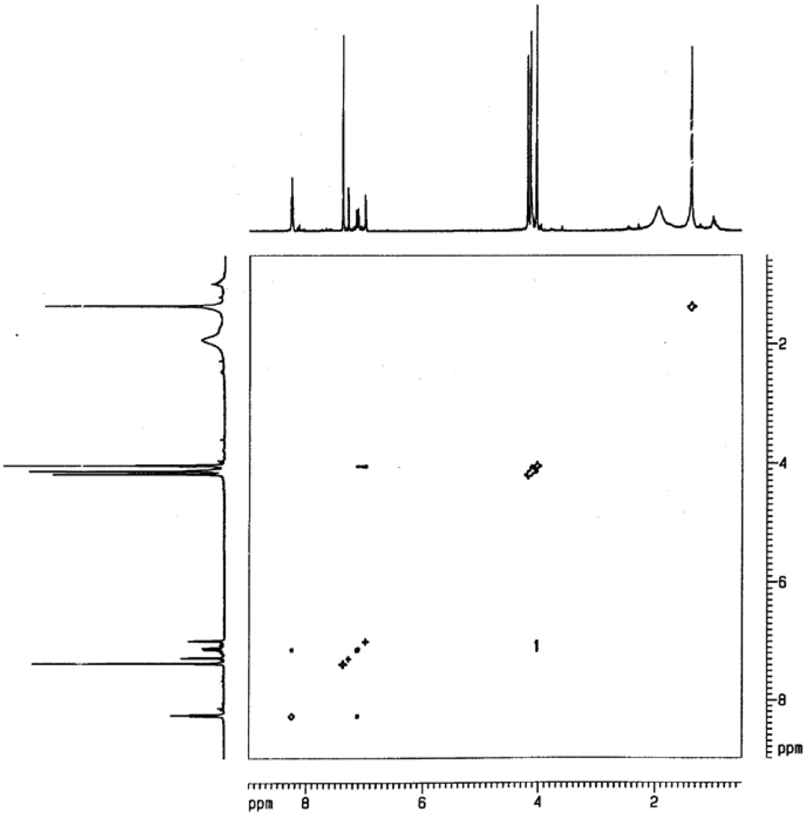

Figure S7. ^{1}H, ^{1}H NOESY-NMR spectrum of **1** (500 MHz, CDCl$_3$).

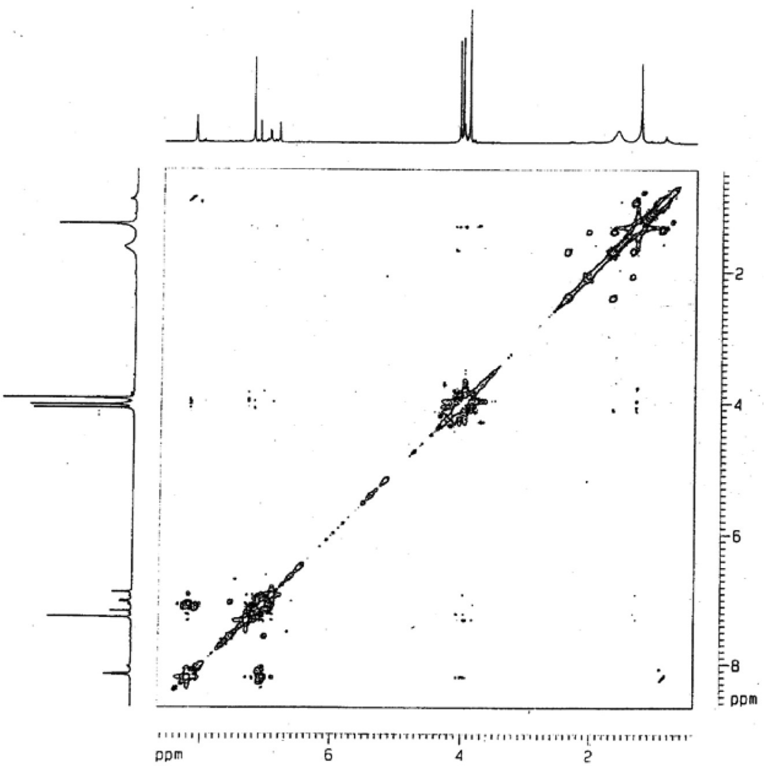

Figure S8. ^{1}H, ^{1}H COSY-NMR spectrum of **1** (500 MHz, CDCl$_3$).

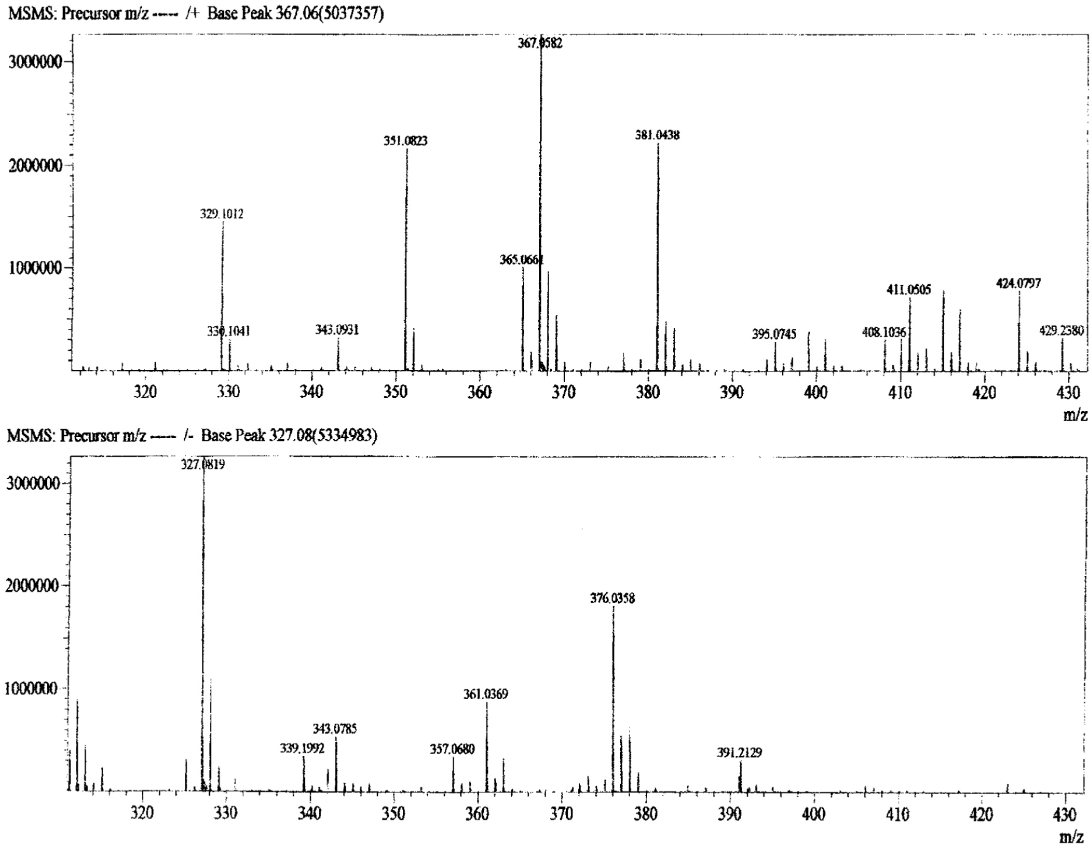

Figure S9. High resolution electrospray ionization mass spectrum of **1.**

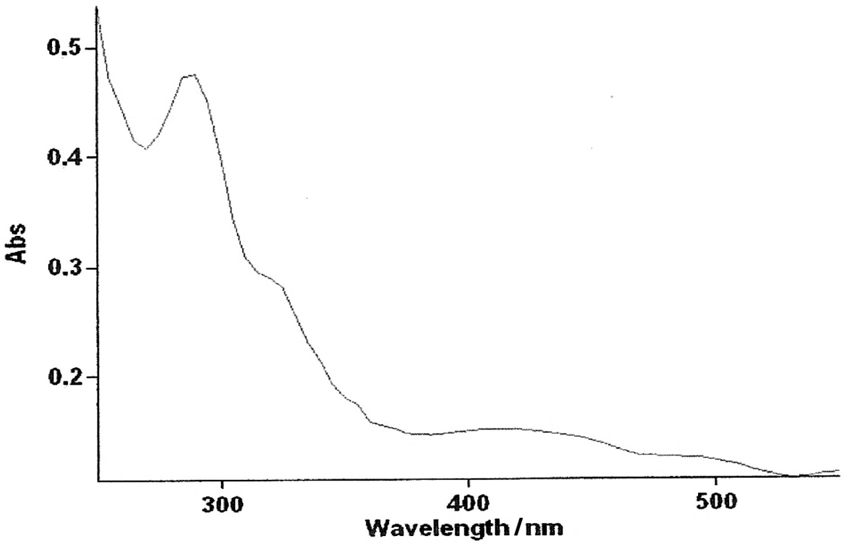

Figure S10. Ultraviolet spectrum of compound **1** (CH_2Cl_2).