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Cinnamoyl Derivatives from *Cordia Platythyrsa* and Chemiotaxonomical Value of the *Cordia* Genus

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Abstract: Phytochemical investigation of the roots and stem barks of *Cordia platythyrsa* (Boraginaceae) had led to the isolation of two new cinnamates, the cordicinnamate **A** compound 1 and the cordicinnamate **B** compound 2 along with four known compounds. Their structures were established by spectroscopic analysis mainly FAB and TOF –MS, ^{1}H NMR and ^{13}C NMR, COSY, HMBC, HSQC and by comparison with literature data. The cinnamoyl derivatives were reported for the first time in the *Cordia* genus. The isolation and identification of cinnamoyl derivatives in *cordia* genus improve the chemiotaxonomy value in this genus.

Keywords: Boraginaceae, *Cordia Platythyrsa*, Cinnamoyl Derivatives, Chemiotaxonomy

1. Introduction

The genus *cordia* belongs to the family of boraginaceae and it is found in warm regions [1]. The decoction of several species of *cordia* genus has been used in traditional medicine to treat influenza, fever, pneumonia, coughs, insomnia, stomach-ache, parasitic [2] and infections [3]. Previous phytochemical investigations of *cordia* genus led to the isolation of pyrrolizidine alkaloids, terpenoids flavonoids, lignans, meroterpenoids naphtoquinones [4]. In addition, phytochemical studies of *Cordia platythyrsa* have revealed the presence of shingolipids, Cordiachromes A-F [5] and xanthones [6]. Its leaves are used for the treatment of convulsions and sleeping sickness (maceration) [7]. With a view to extending the phytochemical investigations of these species, the present paper report the isolation and structure characterization of two new cinnamates namely cordicinnamate A-B and other known compounds.

2. Experimental

2.1. General Experimental Procedure

Melting points were determined on a Büchi 434 melting point apparatus and were uncorrected. ^{1}H NMR (400 MHz) and ^{13}C NMR (150MHz) spectra were recorded at room temperature in $CDCL_3$ using a Bruker AVANCE AM 400 and AMX 500 NMR instruments. Chemical shifts are given in δ (ppm) value relative to TMS as internal standard. ESI-TOF mass spectra operating in positive mode were recorded on a finnigan MAT 312 and FAB mass spectra was recorded on Jeol JMS HX 110 mass spectrometer. Silica gel (230-400 meshes) and sephadex gel (LH-20) were used for Column Chromatography (CC) and vacuum liquid chromatography (VLC). Thin Layer Chromatography (TLC) was performed on precoated silica gel plates (60 F254, Macherey-Nagel) using the system solvent n-hexane – EtOAc (9.2:0.8, 8:2) and EtOAc-MeOH (6.5:3.5) as eluent. Spots were visualized by UV light (λmax = 254 nm, 366 nm) and were observed after using sulphuric acid (50%) as spraying reagent.

2.2. Plant Material

The stem barks and roots of *Cordia platythyrsa* were collected in Yaoundé town (Cameroon) and were identified by Dr N. Tsabang, of the Centre for Study of Medicinal Plants of Yaoundé (Cameroon). One voucher specimen ($N^0$43625/HNC) was deposited at the National Herbarium of Cameroon (NHC).

2.3. Extraction and Isolation

The powdered roots (2 Kg) were extracted with CH_2Cl_2-MeOH (1:1) at room temperature for 72 hours. The resulting extract was evaporated to dryness under reduced pressure to yield a dark residue (12.72 g). This residue was partitioned with n-hexane, EtOAc and MeOH. The EtOAc extract was evaporated under reduced pressure to afford 8 g of residue. This residue was submitted to vacuum liquid chromatography (VLC) on silica gel 230-400 meshes eluted with n-hexane – EtOAc and EtOAc in order of increasing polarity. As result, 3 fractions (S1, S2 and S3) were collected on the basis of TLC. Fraction S3 was subjected to CC using silica gel 230-400 meshes eluted with n-hexane – EtOAc (9.2:0.8) afforded to 9 subfractions. Subfraction S375 was purified using sephadex gel LH-20 eluted with MeOH to afford compounds 1 (1.90 mg) and 5 (2 mg).

The powdered stem barks (6.5 Kg) were extracted with CH_2Cl_2-MeOH (1:1) at room temperature for 72 hours. The resulting extract was evaporated to dryness under reduced pressure to yield a dark residue (200 g). This residue was partitioned with n-hexane, EtOAc and MeOH. The EtOAc extract was evaporated under reduced pressure to give 97 g of residue which was in turn submitted to vacuum liquid chromatography (VLC) on using silica gel 230-400 meshes eluted with n-hexane – EtOAc, EtOAc and EtOAc- MeOH in order of increasing polarity. As result, 7 fractions (B0, B1, B2, B3, B4, B5 and B6) were collected on the basis of TLC. Fraction B3 and B4 were subjected to CC purification using silica gel 230-400 meshes eluted with n-hexane – EtOAc (8:2) to give compounds 2 (2mg), 3 (2mg) and 6 (3mg). Fraction B6 was subjected to CC purification using silica gel 230-400 meshes eluted with EtOAc- MeOH (6.5:3.5) afforded to 4 (20mg).

3. Results and Discussion

3.1. Identification of the Compounds

Compound 1 was obtained as a white powder. Its molecular formula was deduced as $C_{28}H_{46}O_3$ by negative mode FAB-MS at m/z = 429.0 $[M-H]^+$. The cinnamoyl moiety was characterized by ^{1}HNMR signals (table 1) at δ_H 6,81 (1H,d, J=8Hz, H-2'), 6.99 (1H, d, J=8Hz, H-3'), 6.97(1H,S, H-5'), 6,21(1H,d, J=16Hz, H-2) and 7.53 (1H, d, J=16Hz, H-3) [8, 9]. The methoxy and methyl group linked to aromatic ring were observed respectively at δ_H 3.85 (3H, S, 4'-OCH_3) and 1.53 (3H, S, 6'-CH_3). Proton signals owing to aliphatic chain were observed at δ_H 1.18(12H, S, H-5''-14''), 4.11(2H, t, H-1'') and 0.81(6H, S, 2x4''-CH_3). The ^{13}C NMR spectrum with signals at δ_C 168,0 (C, C-1), 114,7(CH,C-2'), 123,1 (CH,C-3'), 109,2 (CH,C-5'), δ 115,7 (CH,C-2) and 144,0 (CH, C-3) had demonstrated the presence of cinnamoyl moiety [8, 9]. Aliphatic chain was identified and characterized by signals at δ 22.7, 31.9, 23.0 (10 CH_2, C-5''-14''), 37.2 (C, C-4''). Protons position of aliphatic chain and cinnamoyl moiety were supported by COSY correlations (figure 1) H-2/ H-3, H-2'/H-3'and H-1''/H-2''. The carbon signals were assigned by HSQC spectrum and were confirmed by HMBC spectrum. Using HMBC correlations (figure 1) of H-3''/C-4''; 4'-OCH_3/C-4'; 6'-CH_3/C-6'and H-1''/C-1, C-2'' had permitted to link aliphatic chain, methoxy and methyl group to cinnamoyl moiety. From the spectral evidences and literature data, the structure of compound 1 was characterized as 1-(4'',4''-dimethylpentadecyl)-4'-methoxy-6'-methyl cinnamate (Cordicinnamate **A**).

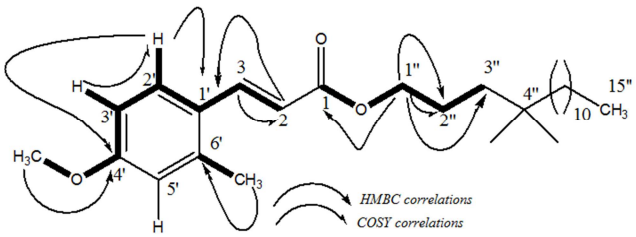


Figure 1. *HMBC and COSY correlations (bold lines) for compound 1.*

Compound 2 isolated as a white powder, exhibited molecular formula $C_{39}H_{68}O_4$ as determined from its positive mode TOF-MS at m/z = 603.5003 $[M+3H]^+$. Comparison of the NMR data (table 1) of compound 2 with those of compound 1 indicated a slight modification in the cinnamoyl moiety of compound 2. Instead of the aromatic proton at C-3' and methyl group at C-6', signals detected were those of an aliphatic chain and aromatic proton at δ_H 1.64 (2H, m, H-1'''), 1.18 (36H, S, H-3'''-21'''), 1.53 (2H, m, H-22'''), 3.53 (2H, t, H-23''') and 7.03(1H, d, J=8 Hz,1.5 Hz, d, H-6') respectively in ^{1}HNMR spectrum. HSQC NMR experiment was used to assign H-1''', H-3'''-21''', H-22''', H-23''' and H-6'. ^{1}HNMR spectrum showed signals at δ_H 3.32 (3H, S, 23'''-OCH_3) characterize methoxy group attached to aliphatic chain and at δ_H 1.48 (2H, m, H-2'') and 1.32 (2H, m, H-4'') attributed to a second aliphatic chain. Protons positions of the above aliphatic chain and cinnamoyl moiety were confirmed by COSY correlations (figure 2) H-2/H-3, H-5'/H-6', H-1''/H-2'' and H-22'''/H-23'''. The HMBC correlation (figure 2) of H-5'/C-1', C-3 and H-1''/C-2'', C-4'' demonstrated the presence of ester group [8, 9]. Thus the structure of 2 was established as 3'-(23'''-methoxy trieicosanyl)-1-(pentyl)-4'-methoxycinnamate (Cordicinnamate B).

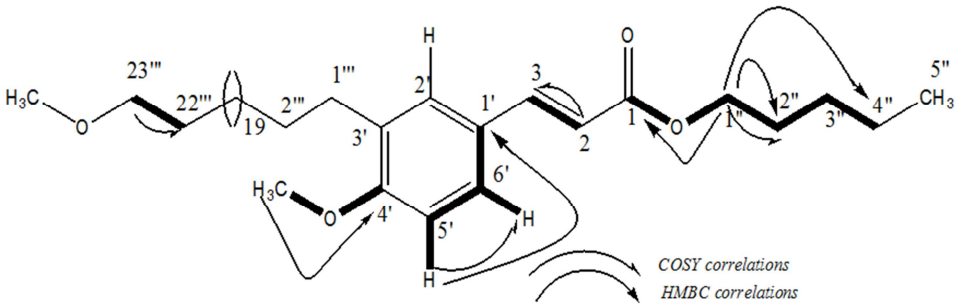
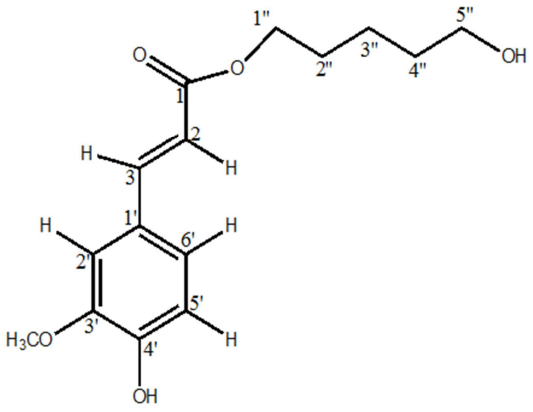


Figure 2. *HMBC and COSY correlations (bold lines) for compound 2.*

Compound 3 was obtained as a white powder. Its molecular formula was assigned as $C_{15}H_{20}O_5$ as deduced from TOF-MS (positive mode) m/z= 282 $[M+2H]^+$. Comparison of the NMR data (table 1) of compound 3 with those of compound 2 indicated the signal at δ_H 3.91 (1H, S, 3'-OCH_3), 5.81(1H, S, 4'-OH) and 3.61(2H, t) instead of aliphatic chain, methoxy and methylene group respectively in ^{1}HNMR spectrum. Its structure (Figure 3) was elucidated by 1D and 2D NMR spectroscopy and it was identified as 1-(5''-hydroxypentyl)-4-hydroxy-3-methoxycinnamate [10]. Structures of the compounds 4-6 were elucidated by 1D and 2D NMR spectroscopy. All the physical and spectral data were identical to the reported values in literature [6, 11-14]. The compounds were identified as methyl orsellinate 4, paramethoxytoylehexanoate 5 and 3-*O*-β-D-glucopyranosyl-β-sitosterol 6 (Figure 3).



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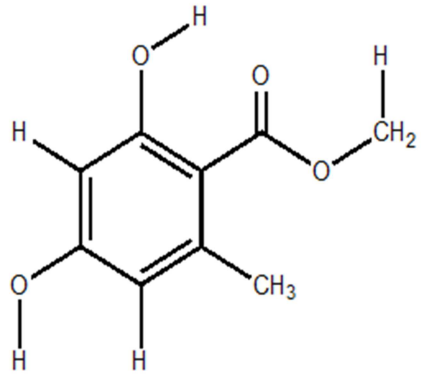

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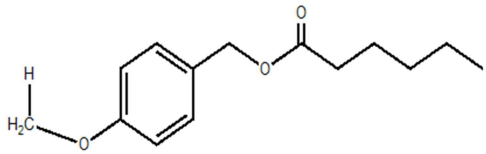

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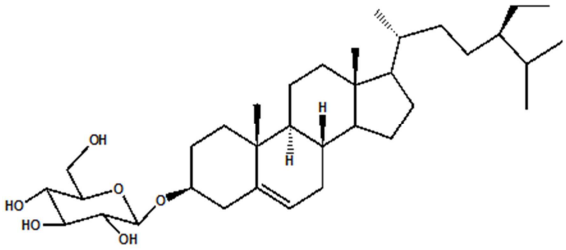

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Figure 3. *Chemical structure of compound 3-6.*

Previous studies of *Cordia* species led to various skeletons of compounds. The triterpenoids have been isolated both from *Cordia verbenacea* DC and *Cordia multispicata* [15] and Dammarane-type triterpenes both from *Cordia spinescens* and *Cordia multispicata* [16]. The Meroterpenoid naphthoquinones have been isolated both from the roots of *Cordia linnaei* and *Cordia corymbosa* [17]. The roots of *Cordia curassavica* [18] and wood of *Cordia fragrantissima* afforded hydroquinones [19]. The magnesium lithospermate, Calcium rosmarinate and magnesium rosmarinate were isolated from the leaves of *Cordia spinescens* [20]. The investigation of the heartwood of *Cordia millenii* yielded terpenoid quinones [21]. Hydroquinone terpenoids were isolated both from *Cordia alliodora* and the heartwood of *Cordia elaeagnoides* [22]. The terpenoid glycosides have been isolated from *Cordia oblique* [23].

In addition, phytochemical studies on *Cordia platythyrsa* yielded to two news cinnamoyl derivatives, Cordicinnamate **A** (compound 1) and Cordicinnamate B (compound 2). To the best of our knowledge this is the first time that cinnamates have been reported from *Cordia* genus.

3.2. Cordicinnamate A (Compound 1)

White powder; MP =116-118°C; ^{1}H NMR ($CDCL_3$, 400MHz) and ^{13}NMR ($CDCL_3$, 150MHz) data see table 1; FAB-MS m/z = 429.0 $[M-H]^+$ (calcd. for $C_{28}H_{46}O_3$, 430.0).

Table 1. *^{1}H NMR (400MHz) and ^{13}NMR (150MHz) data for compounds 1-3 in $CDCL_3$.*

1			2		3	
Position	δ_C	δ_H[mult, J (Hz)]	δ_C	δ_H[mult, J (Hz)]	δ_C	δ_H[mult, J (Hz)]
1	168.0	-	168.0	-	167.0	-
2	115.7	6.21 (1H, d, J =16Hz)	115.0	6.21(1H, d, J =16Hz)	117.0	6.27(1H, d, J =15.5Hz)
3	144.0	7.53(1H, d, J =16Hz)	144.0	7.57(1H, d, J =16Hz)	144.0	7.58(1H, d, J =15.5Hz)
1’	127.0	-	127	-	127.0	-
2’	114.7	6.81(1H, d, J =8Hz)	109.0	7.00(1H, d, J =1.5Hz)	109.0	7.01(1H, d, J =1.6Hz)
3	123.1	6.99(1H, d, J =8Hz)	148	-	146.0	-
4’	147.0	-	147.0	-	115.0	-
5’	109.2	6.97(1H, S, 1H)	114.0	6.76(1H, d, J =8Hz)	123.0	7.05(1H, d, J =8Hz)
6’	135.0	-	122.5	7.03(1H, d, J =1.5Hz, 8Hz)	116.0	6.86(1H, d, J =1.6Hz; 8Hz)
3’-OCH_3	-	-	-	-	56.0	3.91(1H, S)
4’-OH		-	-	-	-	5.81(3H, S)
4’-OCH_3	55.9	3.85(3H, S)	56.0	3.85(3H, S)	-	-
6’-CH_3	28.8	1.53(3H, S)	-	-	-	-
1”	64.6	4.11(1H, t,)	64.6	4.11(2H, t)	64.5	4.16(2H, t,)
2”	26.0	1.60(2H, m)	29.0	1.48(2H, m)	30.0	1.6(2H, m)
3”	28.0	0.86(2H, m)	23.0	1.28(2H, m)	26.0	1.2-1.5(2H, m)
4”	37.2	-	26.0	1.32(2H, m)	25.9	1.5(2H, m)
5”	-	-	14.0	0.81(3H, t)	64.0	3.61(2H, m)
5”-14”	22.7, 23.0, 31.9	0.71-0.86(12H,m)	-	-	-	-
15”	14.2	0.78(3H, m)	-	-	-	-
4”-CH_3	19.4	0.75(3H, m)	-	-	-	-
4”-CH_3	18.8	0.75(3H, m)	-	-	-	-
1”’	-	-	34.5	2.20(2H, t)	-	-
2”’	-	-	28.0	1.64(2H, m)	-	-
3”’-21”’	-	-	23.0	1.18(36H, S)	-	-
22”’	-	-	25.0	1.53(2H, m)	-	-
23”’	-	-	62.5	3.53(2H, t)	-	-
23”’-OCH_3	-	-	49.5	3.32(3H, S)	-	-

3.3. Cordicinnamate B (Compound 2)

White powder; MP =185°C; ^{1}H NMR ($CDCL_3$, 400MHz) and ^{13}C NMR ($CDCL_3$, 150MHz) data see table 1; TOF-MS m/z = 603.5003 $[M+3H]^+$ (calcd. for $C_{39}H_{68}O_4$, 600.5003).

3.4. 1-(5”-hydroxypentyl)-4-hydroxy-3-methoxy Cinnamate (Compound 3)

White powder; MP = 63-64°C; ^{1}H NMR ($CDCL_3$, 400MHz) and ^{13}C NMR ($CDCL_3$, 150MHz) data see table 1; TOF-MS m/z= 282 $[M+2H]^+$ (calcd. for $C_{15}H_{20}O_5$, 280.0).

4. Conclusion

Phytochemical studies on *Cordia platythyrsa* yielded two cinnamoyl derivatives isolated for the first time on *Cordia* genus along with five others known compounds. To the best of our knowledge, this is the first time to isolate the cinnamoyl skeleton on the *Cordia* genus. The isolation and the identification of cinnamoyl derivatives in *cordia* genus improve the chemiotaxonomy value of the *Cordia* genus. Further studies aiming to isolate and identify compounds for the other fractions are needed.

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