

TWO NEW DIARYLESTERS FROM *IPOMOEA CAIRICA*

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Abstract

Ipomoea cairica L. Sweet, used in Brazilian folk medicine for curing rheumatism and inflammations. Two new compounds cairicate (**1**) and methoxycairicate (**2**) were isolated from the ethyl acetate extract from *I. cairica* together with one known compound myristyl alcohol reported for the first time from this plant. The structures of compounds were elucidated through spectrometric methods.

Keywords: *Ipomoea cairica*, cairicate, methoxycairicate.

INTRODUCTION

Ipomoea cairica belongs to a Convolvulaceae family. It is a climbing herb and distributed in tropical and subtropical regions. *Ipomoea* species have antimicrobial, spasmolytic, anti-inflammatory, antipyretic and anticancer activities (Rong-Jyh *et al.*, 2008). It is used in Chinese medicine for the treatment of tuberculosis, cough, asthma, acute and chronic viral hepatitis type B, liver cirrhosis and jaundice (Chunyu 2004, Benfen and Liming, 2009, Shangen *et al.*, 2009, Zhiping, 2004 and Shangen *et al.*, 2009).

Lignans isolated from this plant have proved to be interesting compounds for their possible antitumor, anti HIV and Ca²⁺ antagonist activity (Zhiping, 2004). Chemical studies of *Ipomoea cairica* led to isolation of lignans, aromatic acids and fatty acids (Rong-Jyh *et al.*, 2008, Paska *et al.*, 1998, Lima and Braz-Filho, 1997, Siems, *et al.*, 2005 and Wilkinson *et al.*, 2006). The present study led to the isolation of two new lignans named as cairicate (**1**) and methoxycairicate (**2**) and a known compound, myristyl alcohol (**3**), which is for the first time reported from this plant.

MATERIALS AND METHODS

The aerial parts of *Ipomoea cairica* were collected from the Karachi University Campus and identified by the taxonomist of department of botany, University of Karachi.

Low-resolution electron impact mass spectra were recorded on Finnigan-MAT-311A mass spectrometer, coupled with PDP 11/34 computer system. High-resolution mass measurements and fast atom bombardment (FAB) mass measurements were carried out on Jeol-JMS-HX 110 mass spectrometer. FAB source using glycerol or thioglycerol as the matrix and cesium iodide (CsI) as internal standard was used for accurate mass measurements. ¹H-NMR spectra were recorded at

400 MHz and the ¹³C-NMR spectra at 75 MHz on Bruker AM-400 nuclear magnetic resonance spectrometers using SiMe₄ as an internal standard.

Column chromatography was performed on silica gel (Si 60, 70-230 mesh E.Merk). For thick layer chromatography, precoated silica gel GF₂₅₄ preparative plates (20×20, 0.5mm thick, E.Merk) were used and purity of samples were also checked on the same precoated plates.

Extraction and Isolation

The shade dried aerial parts of *Ipomoea cairica* (3 kg) were soaked in ethanol and extraction was repeated thrice at room temperature. The ethanol extract was concentrated under reduced pressure. The gum obtained was dissolved in water and extracted with *n*-hexane, ethyl acetate and methanol successively.

The ethyl acetate fraction (22.65gm) was subjected to vacuum liquid chromatography (VLC) on silica gel (60 F₂₅₄, E. Merk). Six fraction were obtained (fraction A, 100% *n*-hexane), (fraction B, *n*-hexane:ethylacetate, 60:40), (fraction C, *n*-hexane:ethylacetate, 20:80), (fraction D, ethylacetate::methanol 80:20), (fraction E, ethylacetate:methanol, 60:40), (fraction F, 100% methanol).

Column chromatography was performed on silica gel (Si, 60, 70-230 mesh, E.Merk). Fraction C was subjected to Column chromatography (CC) over silica gel. The column was eluted with *n*-hexane / ethyl acetate and ethyl acetate / methanol gradient system in increasing order of polarity yielding 63 fractions. Fraction 21 exhibited two major spots which were purified through preparative TLC plates (Chloroform : Methanol, 8:2) resulting in the isolation of 0.020 g of **1** and 0.015g of **2**. Compound **3** (0.08 g) was obtained from fraction B as a white crystals after purification through prep. TLC (hexane: ethylacetate, 8:2) .

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RESULTS

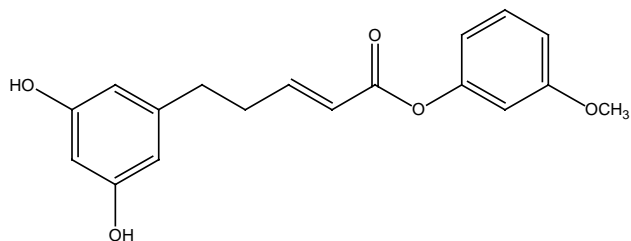
Methoxycairicate (1). White crystals (yield 20 mg). Rf: 0.77 (CHCl₃ : MeOH : 8 : 2).

¹H-NMR (CD₃OD, 300 MHz) δ: 7.45 (d, *J*=1.8 Hz), 7.40 (d, *J*=1.8 Hz), 7.11 (d, *J*=1.8 Hz), 7.05 (d, *J*=8.4 Hz), 6.78 (dd, *J*=8.1, 2.7 Hz), 6.70 (dd, *J*=8.7, 2.7 Hz), 6.41 (d, *J*=15.9 Hz), 6.35 (d, *J*=15.9 Hz), 3.877 (s, OCH₃), 3.45 (dt, *J*=14.7, 7.5 Hz), 2.74 (t, *J*=7.5 Hz). ¹³C-NMR (CD₃OD, 75 MHz) δ: 169 (C-1), 156.96 (C-3'), 142.03 (C-3), 141.78 (C-3'', 5''), 131.31 (C-1'), 130.74 (C-4'), 130.56 (C-5'), 128.29 (C-1''), 123.22 (C-2), 118.74 (C-2'), 116.47 (C-6'), 116.27 (C-2''), 115.82 (C-6), 111.56 (C-4), 56.39 (-OMe), 42.56 (C-5), 35.82 (C-4). EIMS *m/z* (rel. int. %): 314 (M⁺, 2.75), 283 (2.58), 192 (55.38), 177 (100.00), 164 (30.26), 137 (2.23), 107 (37.83).

Cairicate 2: White crystals (yield 15 mg). Rf: 0.75 (CHCl₃ : MeOH : 8 : 2). ¹H-NMR (CD₃OD, 300 MHz) δ: 7.45 (d, *J*=1.8 Hz), 7.40 (d, *J*=1.8 Hz), 7.11 (d, *J*=1.8 Hz), 6.41 (d, *J*=15.9 Hz), 6.35 (d, *J*=15.9 Hz), 3.45 (dt, *J*=14.7, 7.5 Hz), 2.74 (t, *J*=7.5 Hz). ¹³C-NMR (CD₃OD, 75 MHz) δ: 169 (C-1), 131 (C-3'), 142.03 (C-3), 141.78 (C-3'', 5''), 131.31 (C-1'), 130.74 (C-4'), 121.56 (C-5'), 128.29 (C-1''), 123.22 (C-2), 118.74 (C-2'), 116.47 (C-6'), 116.27 (C-2''), 121.82 (C-6'), 126.56 (C-4), 42.56 (C-5), 35.82 (C-4). EIMS *m/z* (rel. int. %): 284 (M⁺, 4.61), 174 (3.2), 147 (100), 163 (4.86), 109 (60), 121 (8.36), 92 (28), 77 (2.1).

DISCUSSION

Compound 1 was isolated as white crystalline solid. The molecular formula was deduced by HR-EIMS showing molecular ion peak at *m/z* 314.11643 (calcd. 314.11544) corresponding to the molecular formula C₁₈H₁₈O₅. The other important peaks were observed at 283 (M-OCH₃)⁺, 192 (M-C₇H₇O₂)⁺, 177 (M-C₈H₉O₂)⁺, 164 (M-C₈H₇O₃)⁺ and 107 (M-C₇H₇O)⁺.



Compound 1

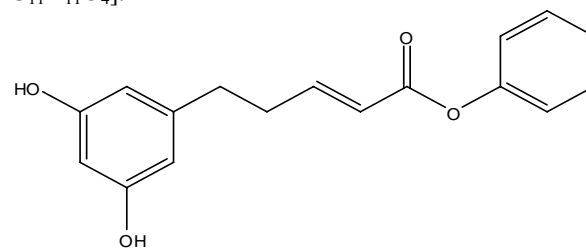
The ¹H-NMR spectrum exhibited 3 doublets at δ 7.45 (*J*=1.8), 7.40 (*J*=1.8) and 7.11 (*J*=1.8) indicating the presence of a trisubstituted benzene ring with *meta* coupled H's. The coupling constants of these hydrogens indicated that the substituents are present at 3 and 5

positions of the benzene ring. Two double doublets at δ 6.78 (*J*=8.1, 2.7 Hz) and 6.70 (*J*=8.7, 2.7 Hz) exhibited the ABX pattern in another benzene ring showing *ortho* and *meta* coupling with H-5 and H-2 of H-4 and H-6 respectively. The presence of two *trans* olefinic protons was indicated by an AB pattern of doublets at δ 6.41 and 6.35 (*J*=15.9 Hz). A doublet of triplet at δ 3.45 (*J*=14.7, 7.5 Hz) and a triplet at δ 2.74 (*J*=14.7, 7.5 Hz) corroborated the presence of two exocyclic methylene groups.

The ¹³C-NMR exhibited eighteen carbon signals. The multiplicity of the carbon signals was established by carrying out BB and DEPT experiments which indicated the presence of one methoxy, two methylene, eight methine, six quaternary and one carbonyl carbon.

In view of the above spectral evidences, the structure of compound 1 was established as 3-methoxyphenyl (*E*)-3-(3,5-dihydroxyphenyl)-2-pentenoate.

Compound 2 was obtained as white solid and the molecular formula was elucidated as C₁₇H₁₆O₄ from the molecular ion peak at *m/z* 284 [M]⁺. Both the ¹H-NMR and ¹³C-NMR spectrum showed a similar signal pattern to that of compound 1 except for the lack of a methoxy signal and appearance of an aryl proton signal which showed AB doublets at δ 7.25 (1H, d, *J*=8.21 Hz, H-2', 6'), 7.39 (1H, d, *J*=8.21 Hz, H-3', 5') and δ 7.15 (1H, d, *J*=7.45 Hz, H-4'). It was also confirmed by EI-MS, the molecular mass of compound 2 revealed the loss of methoxy from 1. The base peak at *m/z* 147 [M-C₈H₉O₂] other fragments are 163 [M-C₇H₅O₂] and 77 [M-C₁₁H₁₁O₄].



Compound 2

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