AN ESTER OF 4-METHOXY CYNNAMIC ACID ISOLATED FROM Xylocarpus moluccensis (Lamk) M. Roem (MELIACEAE)

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ABSTRACT

An ester derivative of 4-methoxycinnamic acid, i.e. 2-ethylhexyl 4-methoxycinnamate was isolated for the first time from the chloroform extract of stem bark of Xylocarpus moluccensis (Lamk) M. Roem (Meliaceae) along with β-sitosterol and stigmasterol. The first structure was elucidated with the help of various spectroscopic techniques, including IR, GC-MS, and NMR spectra. Two last structures were determined by comparison with the reported compounds in literature. These compounds were also found in the hexane extract of the plant.

Keywords: Ester of 4-methoxycinnamic acid; β-sitosterol; stigmasterol; Xylocarpus moluccensis

INTRODUCTION

Meliaceae contains various types of compounds, especially pentacyclic triterpenoid and limonoids [1]. As known that Xylocarpus genus belongs to the family Meliaceae, therefore the plant can be predicted consisting of the compounds. The plants belonging to Xylocarpus genus are composed of 3 species, i.e., X. granatum, X. moluccensus and X. rumphii. According to information from NAPRALERT database developed by University of Illinois at Chicago, several types of compounds present in plants of Xylocarpus genus can be classified into groups as follows: carbohydrates, glyceride ester, isoquinoline alkaloids, quinolone alkaloids, phenolic compounds, secoiridoid monoterpenes, steroids, and triterpenes.

Literature research on chemical constituents consisted of X. moluccensis reported that the species contain type of monoterpenoid and limonoid compounds, with marker compound, i.e. Xylomollin and Xyloccensin 1,2 [2]. Continues phytochemical research on the wood of the plant have obtained three new limonoids, i.e. xyloccensins G, H, and I [3]. Two new limonoids, namely xyloccensin I and xyloccensin J, have also been isolated from the plant and X. granatum [4-5].

Past our investigations on the chemical constitutes of the stem bark of mangrove plant, X. moluccensis (Lamk) M. Roem), one of Meliaceous plants, have yielded two steroidal compounds, i.e. stigmasterol (2) and β-sitosterol (3) from hexane extract [6]. As part of our continuing search for bioactive insecticidal natural products from mangrove plants [7], we now just describe the isolation and structural elucidation of an ester derivative of cinnamic acid, named 2-ethylhexyl 4-methoxycinnamate (1) belonging to be a phenolic compounds from chloroform extract of X. moluccensis.

EXPERIMENTAL SECTION

Materials

Powdered and dried samples used in this research is X. moluccensis, especially stem bark was

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Fig 1. IR Spectrum of Compound 1

isolated compound (1) was measured by using IR spectrophotometers with Buck Scientific M500. $^1$H- and $^{13}$C-NMR using spectrometer of JEOL JNM-AL300/AL400 FTNMR, operated at 399.65 MHz ($^1$H) and 100.40 MHz ($^{13}$C), with tetramethylsilane as internal standard, and spectrometer of GC-MS Shimadzu QP-2010S. Melting point of compound 1 was determined on Electrothermal Apparatus.

Procedure

The milled and dried stem bark (3 kg) of X. moluccencis was extracted with chloroform (10 L) for 24 h and the process was repeated three times. The chloroform extract, on removal of the solvent under reduced pressure by evaporation, gave a brown residue (15 g). A portion (7.5 g) of the total chloroform extract were subjected by VLC using hexane-ethyl acetate system (100:0 ~ 0:100) followed by methanol to yield 14 fractions. This chromatographic step was repeated twice on portions of 7.5 g each of the chloroform extract. Five primary fractions were ultimately obtained on combining the eluates on the basis of TLC. The second fraction (2.3 g) was again fractionated by GCC using hexane : ethyl acetate (96:4) to yield 57 fractions. Furthermore, the fractions can be grouped on the basis of TLC to give 6 fractions, i.e., fraction A (1-9), B (10), C (11-25), D (26), E (27-35), and F (36-57). Fraction A (1-9) is allowed in open room to give yellowish residue. Next, the residue is crystallized from hot methanol to yield a white crystal as compound 2 and 3 to be a mixture (30 mg). When performed by Liebermann-Burchard reagent, the mixture gave blue color indicating the presence of steroidal compounds. Then, the fraction D (26) was evaporated occurred a white precipitate. The precipitate was, then purified by recrystallization using hexane to afford compound 1 as needle white crystal (pure enough) (10 mg). The purity of the compound 1 can also be shown by GC-MS chromatogram (see Fig. 3). When tested by FeCl$_3$ 1% (in methanol), it showed pale yellow color indicating the presence of phenolic compound.
RESULT AND DISCUSSION

2-Ethylhexyl 4-methoxycynnamate (1)

Needle white crystalline form, m.p. 35–36 °C. -IR (KBr) \( \nu \) (cm\(^{-1}\)) = 2925.3, 2859.5, 1703.7, 1603.3, 1511.9, 1467.4, 1253.4, 1165.6, and 821.3 cm\(^{-1}\) (see Fig. 1). 

Compound 1 was obtained as needle white crystalline form, m.p. 35–36 °C. Its molecular formula was established as C\(_{18}\)H\(_{26}\)O\(_3\) in which Double Bond Equivalence (DBE) is five (5) consisting of 1 benzene ring and 1 unsaturated carbon-carbon unit. The IR indicated the presence of aliphatic (2925.3 and 285.5 cm\(^{-1}\)), ester carbonyl group (1703.7 cm\(^{-1}\)), aromatic (1603.3, 1511.9, and 1467.4 cm\(^{-1}\)), oxygenated benzene (1253.4 cm\(^{-1}\)), alkyl ester (1165.6 cm\(^{-1}\)), and 1,4-disubstituted benzene (821.3 cm\(^{-1}\))
The evidence of the data is supported by GC-MS (m/z: 290) (C_{18}H_{26}O_{3}) (see Fig. 4) and NMR data (see Table 1).

The analysis of its NMR data, including NMR one dimension (1H- and 13C-NMR) and two dimension (HMQC spectrum only), allowed for an unambiguous assignment of proton and carbon signals (see Table 1). The 1H-NMR spectrum of 1 displayed two sets of ortho-coupled aromatic proton signals in 2,3-(5') spin system for the presence of one –methoxyphenyl group at δ 6.90 [2H, d, J = 8.4 Hz, H-3'(5')], 7.48 d [2H, d, J = 8.4 Hz, H-2'(6')]. The 1H-NMR spectrum of 1 also indicated the presence of a set of trans configuration at δ 6.36 (1H, d, J = 16.0 Hz, H-2) and 7.64 (d, J = 16.0 Hz, H-3).

The 13C-NMR spectrum of 1 displayed the presence thirty four signals representing significant eighteen carbons, consisting of 9 sp3 carbon signals at δ 55.4 (-OMe), 64.6 (C-1'), 31.8 (C-2'), 29.2 (C-3'), 28.8 (C-4'), 26.0 (C-7'), 22.6 (C-5'), and 14.1 (C-6'(8')) ppm, and 9 sp2 carbon, including one α,β-unsaturated carbonyl at δ 167.4 (C=O), 144.2 and 115.8 (C=C) and one oxyaryl carbon at δ 161.3 (C-4'), 132.1 (C-1'), 129.7 (C-2'(6')), and 114.3 (C-3'/5'). These spectral data indicated that 1 is an ester of 1,4-disubstituted cynnamic acid as part of the structure attached an alkyl. The complete assignment of the protonated carbon was confirmed by means of HMQC spectrum (Fig. 2). The NMR data were consistent with 2 Ethylhexyl 4-methoxycynnamate. The proposed compound 1 is supported by small detail data of GC-MS fragmentation as presented in Fig. 5.

CONCLUSION

An ester derivative of 4-methoxy cynnamic acid, namely 2-ethylhexyl 4-methoxycynnamate was isolated from chloroform extract of Xylocarpus moluccensis (Lamk) M. Roem (Meliaceae) along with stigmasterol and β-sitosterol. This is the first report of the chemical constituents of this species, and the type of compound isolated was in accordance with the established information of Xylocarpus genus.

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