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Cinnamic Acid Derivate From the Bark of *Lerchea bracteata* Val.

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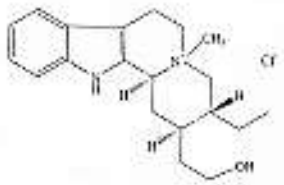
Abstract

Penyelidikan kandungan kimia dari batang tumbuhan *Lerchea brateata* Val telah dilakukan dan berhasil mendapatkan senyawa asam 3,4-dihidroksisinamatmetil ester yang diisolasi dari fraksi etil asetat menggunakan metoda kromatografi. Senyawa ini dimurnikan melalui proses rekristalisasi dan berbentuk kristal kekuningan dan meleleh pada 162-163 °C. Struktur dielusidasi melalui interprestasi spektrum UV, IR serta spektrum ^{1}H dan ^{13}C RMI (COSY, HMBC/HSQC). Bobot molekul diperoleh dari hasil spektrum masa.

Keywords: *Lerchea bracteata* Val, Rubiaceae, 3,4-dihyroxymethylcinnamic acid

Introduction

Lerchea bracteata Val (Rubiacece) is one of species growing in West Sumatra and locally named as "Sitapuung Rimbo". No traditional value has been recorded so far However, people in the region are used it occasionally for pain releaving or treatmen of skin illines (Axelius, 1987; Arbain *et.al*,1999). Most of any part of the plants were positive test with Mayer's reagent (Farnworth, 1966; Arbain *et.al*,2001). From our previous study, methanolic extract of the leaves were obtained a new quartenary alkaloid indol and named as Lerchein (I) (Arbain, *et al*, 1992)



(I)

As a part of our systematic examination on chemical constituent of this plant, the bark *Lerchea bracteata* Val was reinvestigated and the result leading to isolation of 3,4-dihyroxy-*trans*-cinnamic acid methyl ester or methyl caffeate (II) which is firstly reported from this species.

MATERIALS AND METHODS

General: Melting point was determined on Fisher melting point apparatus and uncorrected. Electronic spectra was determined from methanol solution using Shimatzu UV-VIS 1601 spectrophotometer. Infrared spectrum was recorded as potassium bromide disc using a Perkin-Elmer 1600 FTIR instrument. Proton and carbon NMR spectra were determined in DMSO on a Bruker AM300 spectrometer at 300 and 75 MHz, respectively. Column chromatography was performed on silica gel G (Merck, 7743) and TLC on silica gel with indicator at 254 nm (Polygram Sil G/UV_{254}, No. 805023).

Plant materials: The bark of *Lerchea bracteata* Val were collected from Kambang village on April 2003, Pesisir Selatan West Sumatra. A voucher specimen was deposited in Herbarium Biology-FMIPA, the University of Andalas (ANDA) with collection number DPP/004/2003.

Extraction and purification: The fresh bark (2 Kg) of *Lerchea bracteata* Val. where chopped into small pieces, were extracted with methanol for 3 days. Extraction was repeated twice more and the combined extracts were concentrated *in vacuo* to about 0.25 lt. The methanolic extract was then adjusted with distilled water to a volume of 0,5 lt and was triturated with hexane and then with ethyl acetate, successively, to separate non-polar compounds and semi polar alkaloid fraction. Water fraction was extracted with n-buthanol. All fraction were evaporated to dryness to give a residu non polar fraction (0,5 g), ethyl acetat fraction (2,1 g) and n-butanol fraction (3,2 g).

Two gram of ethyl acetat fraction were chromatographed on column chromatography using silica gel G and eluted successively with ethyl acetate-methanol mixes of increasing polarity. The fraction with similar Rf value on TLC was combined and rechromatographed using similar solvent system. One band (81 mg) which is still contain small impurities was purified with radial chromatography using n-heksan-chloroform afforded a yellowish

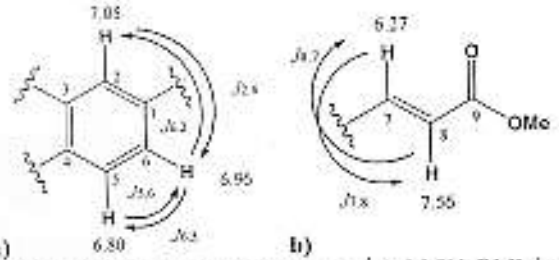
crystalline of 3,4-dihyroxy-*trans*-cinnamic acid methyl ester (48 mg), m.p. 162-163 °C (compound II).

Results and Discussion

The methanol extract of the stem of *Lerchea bracteata* was submitted to solvent partition and the ethyl acetate fraction was chromatographed over Si gel column using n-hexane with increasing polarity by ethyl acetate and then methanol. A major band with similar Rf value was combined and recromathographed ones more and then followed by radial chromathography. After recrystalization on n-hexane-chloroform, a yellowish needle of compound II was obtained (48 mg), m.p. 162-163 °C.

The structure of compound II was established from ^{1}H and ^{13}C NMR spectral data. The IR spectra of (II) showed -OH fungtional group (3493 cm^{-1}), a carbonyl C=O which appear at lower frequency due to conjugate ethylen double bond (1681 cm^{-1}) and an C-H aromatic ring (3308 cm^{-1}) and C=C aromatic (1603 cm^{-1}) (Harbone, 1994). The UV spectra (in MeOH) of (II) present the absorption maxima at 328, 300, 244 and 219 nm showing a characteristic UV absorption of cinnamic derivate.

The ^{1}H NMR spectra (Table 1) showed the presence of specific assignment for proton in aromatic region with signal at 6,80 – 7,05 ppm. The signal at 6,80 and 6,96 with closely related coupling constant (*d*, 7,5 Hz) indicating the present two proton aromatic in ortho position each others. The signal at 6,96 is coupled with proton in para position (*dd*, 2 Hz) and this proton it self appear as singlet at 7,05 ppm. The signal siglet (*s*) at 3,77 ppm was $-OCH_3$ with integration which is represent 3H. The methoxy was shifted to downfield due to the methyl link directly to carbonyl. Two similar doublet signals (*d*) with coupling constant quite large (16,5 Hz) was characteristic for proton ethylene in trans position and this assigment was confirmed by COSY data where H at δ 6.27 ppm has corelate with H at δ 7.56 ppm. (Fig.1.). The ^{1}H-NMR data of the compound II was quided us and it is similar with those of cinnamic acid derivate.



a) b)

Fig 1. Proton-proton corelation of ^{1}H-COSY RMI in aromatic region (a) and double bond ethylene group (b)

Table 1. ^{1}H-NMR of Compound II in CD_3OD

H	δ ppm	Assigment (Hz)
2	7,05	CH, *d*, 1,5 Hz
5	6,80	CH, *d*, 7,5 Hz
6	6,96	CH, *dd*, 2 ; 8 Hz
7	7,56	CH, *d*, 16 Hz
8	6,27	CH, *d*, 16,5 Hz
10	3,77	OCH_3, *s*, -

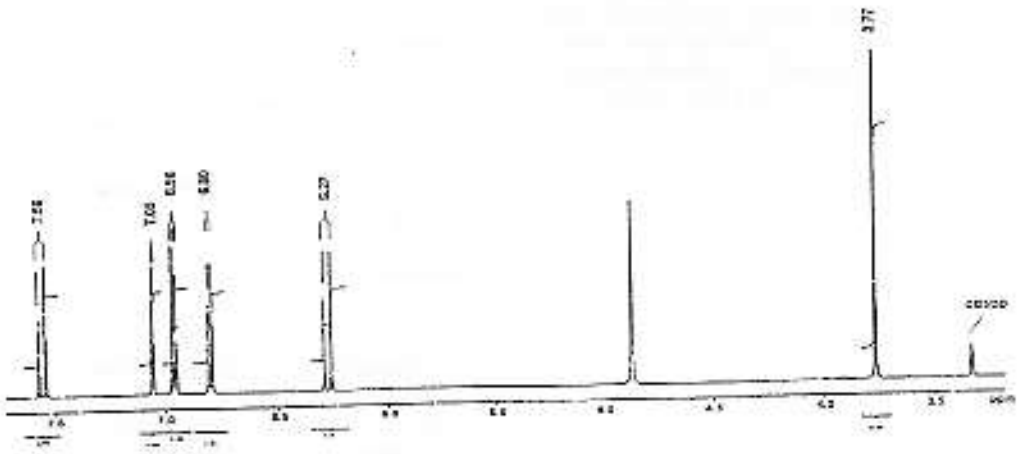


Fig. 2. ^{1}H NMR spectra of Compound II in CD_3OD

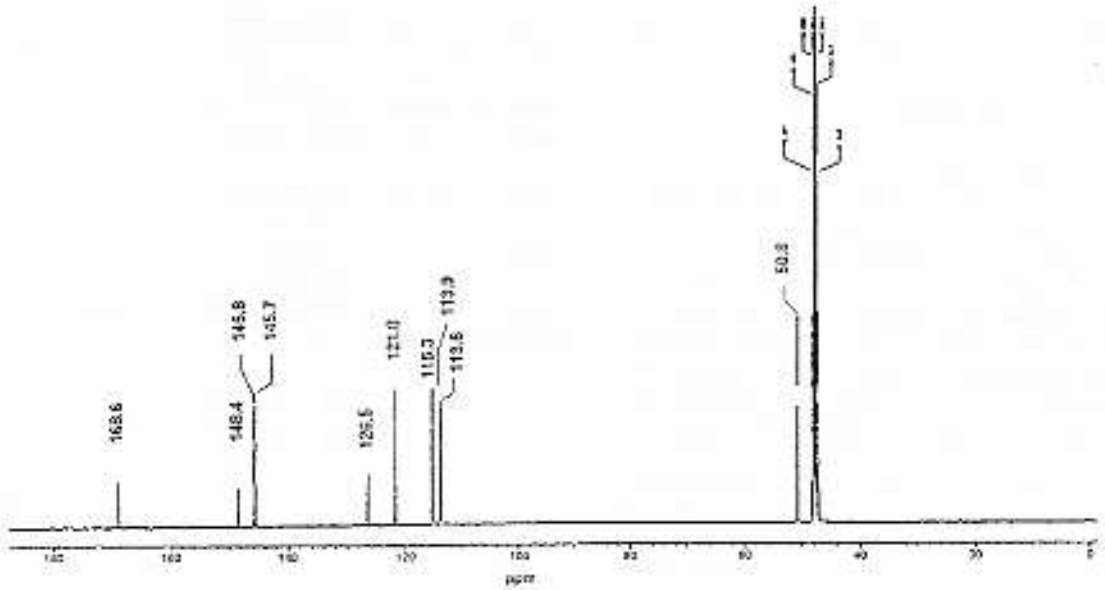
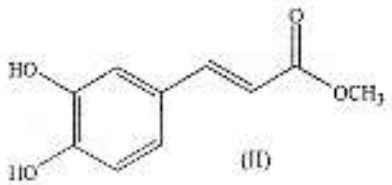


Fig.3 ^{13}C NMR of Compound II in CD_3OD

From ^{13}C NMR spectrum (**Table. 2, Fig.3.**) it is showed the presence of 10 atom carbon signals. The multiplicities of the carbons determine by DEPT led to the attribution of 4 C, 5 CH and 1 CH_3. The signal at δ 168 ppm was attributed to carbonyl. The signals at δ 145.8 and 113.6 ppm were assigment for olefinic carbon double bond and their corelation with the proton signal at δ 7.56 and 6.27 ppm confirmed with HSQC data. As EI MS measurement showing gave the molecular formula (M^+: 197.7), then allowing us to propose the molecular formula $C_{10}H_{10}O_4$

The HMBC spectra showing that the carbon signal at δ 50.8 ppm (CH_3) was coupled with the signal at 168.5 ppm confirming the methoxy attaced to carbon carbonyl. These data were similar with known phenolic methyl caffeate which has been isolated in *Gaillardia pulchella* (m.p. 161-162.5 °C: Inayama, *et.al*, 1984). The structure of compound II is drown as follow:



(II)

Table 2. ^{13}C-NMR of Compound II in CD_3OD

C	δ ppm	Assigment
1	126.5	C
2	113.9	CH
3	145.7	C
4	148.4	C
5	115.3	CH
6	121.8	CH
7	145.8	CH
8	113.6	CH
9	168.6	C
10	50.8	O-CH_3

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