

Propylethanoate Derivative from Coconut Coir

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Abstract: The extraction of the mesocarpic fibre (coir) of dried coconut (*Cocos nucifera*) husk was carried out with n-hexane, ethyl acetate and ethanol in succession using soxhlet extraction method. The crude extract from the coir was separated into fractions using column chromatography and each fraction purified using thin layer chromatography tlc. The components were characterized with the aid of UV-Visible and FT-IR spectroscopic techniques. The structure of the isolated compound was elucidated using various techniques of ¹H-NMR and ¹³C-NMR. The new compound, not yet reported in literature is identified as propyl (2-nitromethylphenyl) ethanoate.

Key words: Coir, coconut husk, tlc, UV-Visible spectrophotometry, extraction method

INTRODUCTION

Coconut (*Cocos nucifera* L.) is a tropical fruit largely consumed in many countries. Coconut palms are abundantly growing in coastal areas of most tropical countries and its wide variety of products is being applied in food and non-food product sectors. Its nutritious nuts represent a major form of livelihood for millions of people (Ohler, 1984, 1999; Batugal *et al.*, 1998). The coconut shell is similar to hard wood in chemical composition being composed mainly of lignin and cellulose. The use of the coconut shell as a source of chemical compounds, mainly to produce phenolic compounds is new and majorly applied in the agriculture and the material industries (Sueli and Gustavo, 2007).

The coir is a coarse fiber extracted from the fibrous outer shell (mesocarp) of a coconut. Coir fibers are found between the husk and the outer shell of a coconut. The individual fiber cells are narrow and hollow, with thick walls made of cellulose. They are pale when immature but later become hardened and yellowed as a layer of lignin is deposited on their walls.

Coir dust is the waste material that remains after the coconut husk has been processed for the extraction of the industrially-valuable long fibers. A portion of the waste material (coir) is processed and used by the rope-making industry, but majority remains unutilized (Suzuki *et al.*, 1998). This waste-grade coir is composed of pithy tissue particles mixed with variable proportions of short to medium-length fibers.

Coconut coir dust is being used successfully for the production of ornamental potted plants (Meerow, 1995; Noguera *et al.*, 1997; Stamps and Evans, 1999) and for

growing other containerized horticultural species (Cresswell, 1992; Teo and Tan, 1993; Offord *et al.*, 1998). World wide, 40-50 million tons of coconuts are grown annually, producing 15-20 million tons of husks (FAO statistics). For coir fibre and fibre products as a commodity, a productivity is estimated of around 700,000 tons year⁻¹ (FAO statistics), which is only a fraction of the otherwise wasted raw material. Since, only a small part of the available husk material is being utilized, new outlets are of interest.

Phytotoxicity and detoxification of fresh coir dust and milled coconut shell have being studied using lettuce bioassay, phytotoxin analysis and incubation with liming and other amendments at different temperatures (Ma and Nichols, 2004). The comparison of the phenolic dependent antioxidant properties of coconut oil extracted under cold and hot conditions have also being carried out (Kapila *et al.*, 2009). The Coconut fiber and cotton waste have being used as substrate for tomato seedlings (Cândido *et al.*, 2007). The wetting effect of the coir has also being studied (Miguel *et al.*, 2008). Patricia *et al.* (2003) studied the influence of particle size on physical and chemical properties of coconut coir dust as container medium. Coconut coir dust particle size affected its physico-chemical and chemical characteristics. Extraction of phenolic compounds from coconut (*Cocos nucifera*) shell powder using ultrasound extraction methods was performed by Sueli and Gustavo (2007). Their results indicated that high amounts of phenolics can be extracted from coconut shell by ultrasound assisted extraction technology. The aim of this research is to isolate and characterize new valuable compounds from the coir of coconut using a cost efficient

method. In continuation of phytochemical investigation of the extract of *Cocos nucifera* coir, we report herein the isolation and structural elucidation of a new propylethanoate derivative. The structure of the isolated compound was verified by means of various techniques of H-NMR and ^{13}C -NMR spectral analysis.

MATERIALS AND METHODS

General experimental procedure: Thin layer Chromatography, TLC plates were examined with a UV lamp operating at a wavelength of 366 nm (long wavelength) and 254 nm (short wavelength). UV-VIS measurements were conducted on an AQUAMATE UV-VISIBLE SPECTROPHOTOMETER V4.60 (Thermal Electron Corporation, Germany). IR Spectra were recorded as a film on sodium chloride disks using NICOLET AVERTEAR 330 FT-IR (Thermal Electron Corporation Spetrum Instrument). For NMR (proton and C-13) measurements, a MERCURY -200 BB NMR SPECTROMETER was used operating at a basic frequency of 200 MHz.

Dried coconut husk (*Cocos nucifera*) was collected in Ilorin, kwara State, Nigeria and identified by the researchers. The outer part of the mesocarp was first cleansed and chopped into small pieces. After separating the fiber (coir) from the powder, the fiber was dried and put into sizeable bits. This was milled and sieved manually to obtain the fine and coarse particles separately and stored at room temperature prior to use. The chemicals and other materials used in the experiment were all analytical grade.

Extraction and isolation procedure: The dried fine and coarse coir (11 g each) was extracted with n-hexane, ethylacetate and ethanol in succession using Soxhlet extraction method. The extract was concentrated to recover the solvent and obtain the solvent-free extract. The percentage yield of the extracts was noted.

Preliminary tests: Some preliminary tests were carried out on the (fine and coarse) crude extracts.

TLC test: The extracts were spotted on TLC precoated plates (Silica gel G_{F254}, 0.25 mm Merck W. Germany). After developing each plate, the plates were dried and examined under the UV-lamp. The spot were noted and the R_f values calculated (James and David, 1976).

Colour visualisation test: This was carried out on the developed TLC plates to know if the components would

give a colour reaction. The plate was sprayed with vanillin reagent freshly prepared according to Olatunji and Sariyu (1989).

Phenol test: This was carried out to confirm the presence of the phenolic compounds by testing with ferric chloride solution. The test was positive.

Isolation: The ethylacetate extracts was chromatographed on a Silical gel column chromatography (diameter 4.2 cm, height 35 cm) using hexane-ethyl acetate (2:1) as eluent to obtain 38 fractions and diethylether-ethanol (1:1) eluent to obtain fractions 39-45. The fractions were checked by TLC (Sigel; hexane-diethylether (1:1), EtOH-Diethylether (1:1)).

The crude hexane extract was also chromatographed on TLC (Si gel, hexane-diethylether (1:1)). No suitable solvent system was found for ethanol crude extract as brown streaks was observed constitiently. The fractions of extracts of both fine and coarse coir materials were found with similar R_f values and characteristic colours and were therefore combined, to afford six fractions (A-F).

A Preparative Thin Layer Chromatography (PTLC) (Glass plates (20×20 cm)) was used to isolate the components of the combined hexane extract. Three distinct spots I, II, III (R_f 0.52, 0.67 and 0.92) as seen on the TLC (Sil gel, Pet. spirit/diethylether (1:1)) was also observed. Each zone was scrapped, extracted with Pet. spirit and concentrated. The three components were re-eluted with Pet. spirit-Diethylether (1:1) on the TLC plate. Component I and II showed four spots each with two corresponding ones. Component III showed only one spot, therefore special attention was given to the component III of the hexane extract.

RESULTS AND DISCUSSION

The infrared spectroscopic analysis of the hexane crude extract shows prominent peaks between 2970-2850 cm^{-1} (O-H str. of carboxylic acid and/or C-H of alkanes); 2730 cm^{-1} (H-C=O of aldehyde); 2360-2340 cm^{-1} (gaseous CO_2 interference); 1740 (C=O); 1710 (C=O of aldehyde conjugated to an aromatic ring); 1460 cm^{-1} (C-H of alkane or nujol peak); 1375 cm^{-1} (C-H bending of alkane); 1300, 1160, 970 and 720 cm^{-1} (C-C finger-print region of alkanes). The diversity of the absorption frequencies is typical of a mixture of compounds.

The IR spectrum of component III of the hexane extract revealed the following major bands: 3820 cm^{-1} (trace of water); 3060 cm^{-1} (=C-H of olefinic or aromatic alkene); 2980-2850 cm^{-1} (C-H of alkanes); 2730 cm^{-1} (amplified nujol peak or C=O of aldehyde); 2360-2340 cm^{-1}

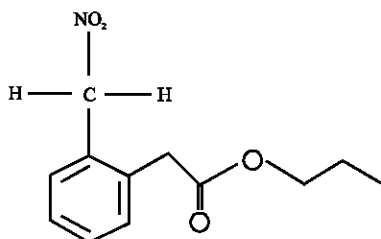


Fig. 1: n-propyl-(2-nitromethylphenyl) ethanoate

(gaseous CO_2 interference); 1730 cm^{-1} ($\text{C}=\text{O}$ of ester); 1600 , 1580 and 1460 cm^{-1} ($\text{C}=\text{C}$ str. and $\text{C}-\text{C}$ of aromatic ring); 1380 cm^{-1} ($\text{C}-\text{H}$ of alkane and aliphatic NO_2); 1290 cm^{-1} ($\text{C}-\text{O}$ str. of ester, fingerprint region of alkane); 1120 cm^{-1} (second $\text{C}-\text{O}$ str. of ester, aromatic $\text{C}-\text{H}$); 750 cm^{-1} (characteristic of an orthodistributed aromatic compound). ^{13}C -NMR of the component III isolated had δ_c 168.0 ppm ($\text{C}=\text{O}$ ester); δ_c 133.0 - 128.0 ppm (aromatic carbons); δ_c 79.0 - 76.0 ppm (solvent peaks i.e., CDCl_3); δ_c 70.0 - 64.0 ppm ($-\text{CH}_2-$ groups) for an electronegative atom and an aromatic ring i.e., $-\text{COOCH}_2-$, $-\text{CH}_2\text{NO}_2$ and $\text{Ar}-\text{CH}_2-\text{CO}-$; δ_c 47.0 ppm ($-\text{CH}_2-$ of an aliphatic group next to an electronegative atom i.e., $-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3$); δ 30.0 ppm ($-\text{CH}_3$).

The ^1H -NMR spectrum showed signal at δ_H 7.8 - 7.2 ppm (aromatic $\text{C}-\text{H}$); δ_H 4.4 - 4.2 ppm (protons next to a nitro group i.e., $-\text{CH}_2\text{NO}_2$); δ_H 2.4 - 2.0 ppm (t of protons next to an electronegative atom and a $-\text{CH}_2$ i.e., $\text{COOCH}_2-\text{CH}_2-$); δ_H 1.8 - 1.6 ppm ($-\text{CH}_2-$ next to an aromatic ring i.e., $\text{Ar}-\text{CH}_2-\text{COO}-$); δ_H 1.4 - 1.0 ppm (m of $-\text{CH}_2-$ of saturated alkane i.e., $-\text{CH}_2-\text{CH}_2-\text{CH}_3$); δ_H 1.0 - 0.7 ppm ($-\text{CH}_3$ next to a saturated alkane). The proposed compound is named n-propyl-(2-nitromethylphenyl) Fig. 1.

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