

Short Communication

Isolation of Polyphenolic Compounds from the Green Coconut (*cocos nucifera*) Shell and Characterization of their Benzoyl Ester Derivatives

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Abstract

Polyphenolic compounds were isolated from the aqueous extract of green coconut shell. Benzoyl ester derivatives were prepared with these polyphenols. Monobenzoyl and dibenzoyl derivatives of a polyphenol were separated and characterized.

Keywords: Green coconut shell; *Cocos nucifera*; Polyphenol.

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1. Introduction

Green coconut (*cocos nucifera*), locally called 'Dab', grows abundantly in all over Bangladesh, especially in coastal region. The water of this green coconut is used as popular soft drinks and the shells are mainly discarded as waste product. The whole or every part of coconut tree is claimed as a dye ware, especially the husk enclosing the matured fruit [1]. Phenol constituent was obtained by destructive distillation of coconut shell at 280⁰C [2]. Coloring materials have been prepared from the extract of coconut shell by coupling with some diazotized compounds. A reddish brown dye was obtained from the coconut shell with the coupling of diazotized 4-H₂NC₆H₄SO₃Na which is useful as a wood stain [3]. Dry distillation of coconut shell fibre followed by ether and alkali extraction and chromatographic separation yielded phenol, p-cresol, caproic acid and p-hydroxy benzoic acid [4]. Preparation of the azo dye from the green coconut-shell extract [5] is also an indication of a source of phenolic compounds. However, no report of the isolation of the chemical components from green coconut is available. Since the green coconut-shell is a waste product in our country, the isolation of phenolic compounds from it and use of these compounds to prepare dye and other valuable products would be

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worthwhile. Therefore, from the point of view of the utilization of unused or waste product, an attempt has been taken in this work to isolate the phenolic compounds from the green coconut shell and to characterize them.

2. Materials and Methods

2.1. Materials

All the reagents and chemicals used for the present work were purchased from BDH (England), FLUKA (Switzerland) and E. MERCK (Germany). Commercial alcohol (Rectified spirit) and absolute alcohol were available from Carew and Company, Darsana, Kushtia, Bangladesh. The solvents were dried and distilled when necessary.

2.1.1. Plant materials

Green coconut is sold in the local market and the shells are thrown away after drinking water. These waste green coconut shells of 6-7 months aged were collected from the local market.

2.2. Methods

A Reichart micro melting point apparatus was used for recording melting point. The UV spectra were recorded on a LKB 4053 Ultraspec K Ultraviolet/Visible spectrophotometer. IR spectra were recorded in KBr discs or in KBr pellets. The ¹H NMR spectra were recorded on a Bruker AM400FT NMR, spectrometers using tetramethyl silane (TMS) as internal standard. The ¹³C NMR spectra were recorded at 125 MHz on a Bruker AM500FT NMR spectrometer. Mass spectra (EIMS) were recorded on a Finigan MAT 312 spectrometer. Fast atom bombardment mass (FAB MS) measurements were conducted in glycerol matrixes on JEOL HX 110 mass spectrometers. TLC was carried out on pre-coated aluminium sheets with silica gel (E-Merck).

The purity of the compounds was tested by analytical thin layer chromatography (TLC) on silica gel 60 GF₂₅₄ cards and the spots were made visible by exposure to UV light. The components of a mixture were separated by preparative thin layer chromatography over silica-gel 60 GF₂₅₄.

2.2.1. Extraction of the green coconut shell-juice

After washing to free from dirt, the shell was cut into pieces and smashed in a wooden mortar to get juice. The juice was then filtered with cloth and paper. Thus, the juice became ready for further treatment.

2.2.2. Identification of the phenolic compounds [6]

The presence of the phenolic compounds in green coconut juice was examined by ferric chloride test. 1 ml of juice was mixed with 1 ml ethyl alcohol and 1 ml 1N HCl. Then 1

drop of 3% FeCl₃ solution was added to this solution. A deep red coloration indicated the presence of phenolic compounds in the juice.

2.2.3. *Preparation of Benzoyl derivatives*

The juice (700 cc) obtained from the green coconut shells was made alkaline with 10% NaOH. Benzoyl chloride was then added to this alkaline juice to obtain benzoyl ester (20.8g). The ester derivatives were then filtered to separate out from the juice.

2.2.4. *Test for benzoyl ester derivatives* [7]

Test for ester: 0.05 gm benzoyl derivative (ester) was dissolved in 1ml ethyl alcohol and 1ml 1N HCl. Then 1 drop 3% FeCl₃ solution was added but no coloration was seen. Then hydroxamic acid test was performed.

Hydroxamic acid test: 0.05gm compounds was taken in a test tube and then 0.05gm hydroxyl amine hydrochloride and 1.5ml 10% NaOH were added and the mixture was boiled for 2 minutes. After cooling and acidification, 2-3 drops of FeCl₃ solution was added. Reddish brown color was appeared, which indicated the presence of ester.

2.2.5. *Separation of the derivatives*

A saturated solution of benzoyl derivative was made in acetone. This saturated solution of benzoyl derivative was fractionated into individual components by column chromatography. The column was eluted with solvent system of petroleum ether: ethyl acetate (3.5:1; 15:1; 10:1; 6:1), petroleum ether: chloroform (3:1; 2:1; 1:1; 1:3) successively. Fractions collected were gathered according to the TLC behavior and four fractions were separated. After evaporation, these fractions afforded four single compounds- compound 1, compound 2, compound 3, and compound 4. Compounds 1 & 2 were found negligible for spectroscopic analysis. Compound 3 (45 mg) and compound 4 (50 mg) were further re-crystallized from methanol and characterized by spectroscopic techniques.

2.2.6. *Spectral analysis of the derivatives*

Two derivatives, compound 3 and 4 were analyzed by IR, ¹H NMR, ¹³C NMR, and Mass spectrophotometers. Data are shown below:

Compound 3

The compound **3** was a white solid, m.p. 139-140 °C. It has the following spectral data:
IR spectra (ν⁻cm⁻¹): 3450, 3433, 1735, 1720, 1263, 1068, 1026.

¹H NMR (δ CDCl₃): 8.10 (m, 4H, Ar-H), 7.9 (m, 2H, Ar-H), 7.54 (m, 4H), 7.25 (s, 1H), 6.20 (m, 2H, Ar-H), 5.74 (s, 2H), 4.90 (s, 2H), 4.86 (s, 1H, OH), 3.99 (s, 3H, OCH₃), 3.07 (s, 3H, OCH₃).

^{13}C NMR : 167.41 (-C=O, 1C), 165.45 (-C=O, 1C), 164.83 (-C=O, 1C), 150.17 (4C), 136.30 (5C), 133.94 (3C), 133.73 (2C), 133.59 (2C), 130.13 (2C), 129.92 (4C), 129.61 (1C), 129.49 (1C), 128.99 (1C), 128.93 (1C), 76.09 (1C), 75.66 (1C), 69.18 (1C), 63.10 (1C).

Mass (m/e): 579 ($\text{M}^+ - 1$), 475 ($\text{M}^+ - 105$), 353, 154, 136.

Compound 4

The compound 4 has the following spectral data:

IR-spectra (cm^{-1}): 3516, 3435, 3406, 1741, 1249, 1026.

^1H NMR (δ CDCl_3): 8.06 (m, 2H, Ar-H), 7.9 (m, 1H, Ar-H), 7.54 (m, 2H), 7.25 (s, 1H), 6.21 (m, 2H, Ar-H), 5.61 (s, 2H), 4.65 (s, 2H), 4.48 (m, 2H, 2-OH), 3.9 (s, 3H, OCH_3), 3.10 (s, 3H, OCH_3).

^{13}C NMR: 166.33 (-C=O, 1C), 164.92 (-C=O, 1C); Aromatic carbons: 150.17, 133.95, 133.87, 133.26, 130.31, 130.10 (2C), 130.06 (2C), 129.94 (2C), 129.64, 129.12, 129.02, 128.69 (2C), 128.64 (3C), 128.47 (2C), Aliphatic carbons: 74.18 (1C), 73.72 (1C), 71.94 (1C), 62.99 (OMe);

MS (m/e): 475 ($\text{M}^+ - 1$), 307, 289, 242, 154, 136.

3. Results and Discussion

The compound 3 shows IR bands at 3450, 3433 cm^{-1} indicating the presence of free hydroxyl group and at 1735 and 1720 cm^{-1} indicate the presence of carbonyl groups. ^1H NMR spectrum indicates the presence of only aromatic (δ 8.10-6.20 ppm) and alkoxy-protons (δ 5.61-3.07 ppm). The compound has roughly about 11 different magnetically equivalent aromatic carbon atoms which are evident also from ^{13}C NMR spectral data. Three carbonyl carbons and four alkoxy carbons are also observed in the spectrum.

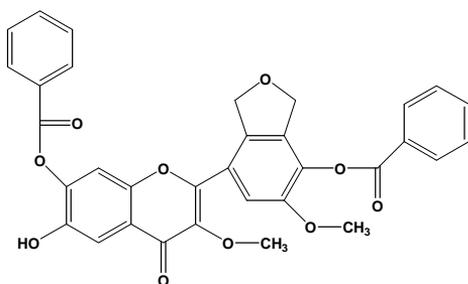


Fig. 1. Compound 3.

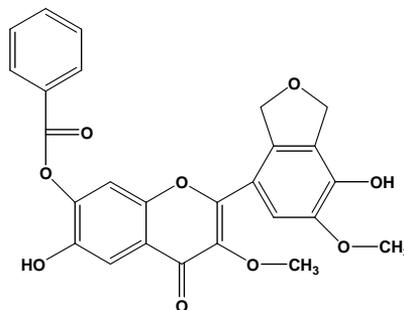


Fig. 2. Compound 4.

Mass spectrum (FAB) shows molecular ion peak corresponding to dibenzoylated derivative of the original polyphenol extract from the natural plant source [Mass (m/e):

579 ($M^+ - 1$)]. Therefore, structure of the compound has been proposed as shown below in Fig. 1 (compound 3).

The same argument may be put forward for the proposed compound 4 (Fig. 2) with only exception that it is a monobenzoylated derivative as evident from the mass spectrum of the compound [Mass (m/e): 475 ($M^+ - 1$)]. However, more ^{13}C peaks are observed for aromatic carbons of this compound which may be due to the less hindrance in the molecule.

4. Conclusion

Two benzoylated derivatives of polyphenolic compounds, extracted from the green coconut (*cocos nucifera*) shell, were prepared and characterized by IR, ^1H NMR, ^{13}C NMR and mass spectral data. In this study polyphenols were separated through derivative preparation. There are a number of phenolic compounds in the coconut shell juice. Further attention should be given to isolate these major phenolic compounds as well as to develop the easy isolation procedure, so that this waste product can be used for the preparation of valuable dye and other important compounds.

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