

Chemical Investigation of the Bark of *Commiphora africana* (Burseraceae)†

M.K. CHOUDHURY*, E.C. JOHNSON AND A.S. AGBAJI¹

Department of Pharmaceutical and Medicinal Chemistry,

Faculty of Pharmaceutical Science, Ahmadu Bello University, Zaria, Nigeria

¹Department of Industrial Chemicals, National Research Institute for Chemical Technology,
Basawa, Zaria, Nigeria

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The methanolic extract of bark of the plant *Commiphora africana* (family: Burseraceae) gave a homogeneous product through chromatographic separation which after crystallization from methanol furnished needles (mp. 142-143°), characterized as dimethylterephthalate (benzene-1, 4-dicarboxylic acid dimethylester), C₁₀H₁₀O₄ (M^r 194) on the basis of spectral analysis (UV, IR, NMR, Mass) and comparison with the synthetic dimethylester prepared from terephthalic acid.

Commiphora africana (A. Rich) Engl. (Family : Burseraceae) is a bushy shrub or small tree (upto 7 metres) with straggling irregular branches, available in drier parts of tropical Africa. Flowers are reddish (October-April), usually appear when the tree is leafless. Fruits (May) are reddish, broadly ellipsoid, practically stalkless, the white stone is surrounded by a resinous pulp. The plant is known as 'Dashi' in Hausa, 'Badadi' in Fulani, 'Kabi' in Kanuri languages in Nigeria. The leaves are pounded with bulrush millet and milk and taken as a stomachic. For scorpion-bite the bark is applied after chewing it along with natron in traditional medicine in Nigeria¹.

We were interested to carry out some chemical investigation and pharmacological studies of the plant. The present article describes the isolation and characterization of dimethylterephthalate, C₁₀H₁₀O₄ (M^r 194), m.p. 142-143° on the basis of spectral (UV, IR, NMR, Mass) and C, H-analysis. The structure was further proven through synthesis prepared from terephthalic acid. The isolation of dimethylterephthalate was reported earlier from other plants²⁻⁵. To the best of our knowledge no phytochemical studies have been reported so far on this plant.

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*For correspondence

All solvents obtained from BDH, England, were distilled before use. Silica gel for column chromatography (M & B Laboratory Chemicals, May & Baker Ltd, Dagenham, England), silica gel for TLC (0.25 mm, E. Merck, Germany) were used for chromatographic separation.

The spots were visualized under UV-lamp at 254 nm. Melting points were determined using Gallenkamp apparatus. The UV spectra were recorded on Pye Unicam 5000 spectrometer SP 8-100.

The plant was collected from a forest near Zaria, Nigeria and authenticated by the herbarium at the Department of Biological Sciences, Ahmadu Bello University, Zaria. The air dried powdered bark (250 g) was defatted with petroleum ether (bp. 60-80°) with Soxhlet apparatus and then extracted with methanol (Soxhlet) for 48 h. The solvent was concentrated to give a red solid material (20 g). The crude extract (1 g) was chromatographed over a column of silica gel (50 g) and elution with CHCl₃-MeOH (9:1) furnished a homogeneous product (80 mg) which after crystallization from methanol yielded crystalline needles, mp. 142-143°.

The compound did not give any colour test; it produced a very faint spot on long exposure in iodine chamber. However, it showed a prominent pink spot under UV lamp at 254 nm.

TLC : $R_f = 0.48$ (benzene), 0.67 (benzene - ethylacetate = 5:1), 0.80 (benzene - ethylacetate = 4:1).

UV (MeOH) : 272 (strong), 292 nm (weak).

IR (Nujol) : 1730 (ester), 1475, 1450 cm^{-1} .

$^1\text{H-NMR}$ (CDCl_3 , 400 MHz, δ) : 3.95 (s, 6H, 2 OCH_3), 8.10 (s, 4H, four aromatic protons).

$^{13}\text{C-NMR}$ (CDCl_3 , 100 MHz, DEPT, δ) : 52.38 (2 CH_3), 129.52 (4 CH), 133.88 (2 QC), 166.24 (2 CO).

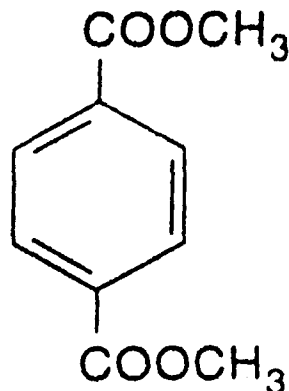
Mass (EI, m/z, %) : $\text{C}_{10}\text{H}_{10}\text{O}_4$, 194 (M^+ , 36), 179 ($\text{M}^+ - \text{CH}_3$, 2), 164 ($\text{M}^+ - 2 \text{CH}_3$, 10), 163 ($\text{M}^+ - \text{OCH}_3$, 100), 135 ($\text{M}^+ - \text{COOCH}_3$, 15), 120 ($\text{M}^+ - \text{CH}_3 - \text{COOCH}_3$, 5), 103 ($\text{M}^+ - \text{COOCH}_3 - \text{CH}_3 \text{OH}$, 9) 76 ($\text{M}^+ - 2 \text{COOCH}_3$, 8).

C, H-analysis : $\text{C}_{10}\text{H}_{10}\text{O}_4$ required : C, 61.85%; H, 5.19%

Found : C, 61.84%; H, 5.25%

Dimethylterephthalate was prepared by refluxing a solution containing terephthalic acid (benzene-1, 4-dicarboxylic acid, 1 g) dissolved in dry methanol (20 ml) and conc. H_2SO_4 (2ml) for 6 h under dry condition (anhydrous CaCl_2 guard tube). The reaction mixture was cooled to room temperature, the precipitated material was filtered, washed with water to remove acid and dried in air (0.9 g). The residue was crystallized from methanol to furnish needles, mp. 142-143°.

The mass spectrum indicated the presence of two methyl ester groups attached, to the benzene ring and their positions were confirmed by NMR (proton and C-13) spectra. The presence of ester group was supported by IR spectrum (1730 cm^{-1}). Two methylester functions situated at 1, 4-positions in the benzene nucleus made the ester groups and four aromatic protons equivalent. This fact was revealed in the proton NMR spectrum which showed two signals at $\delta 3.95$ (OCH_3 from COOCH_3) and at $\delta 8.10$ (aromatic). It was further supported by the C-13



NMR spectrum where two equivalent methyl (2 CH_3) groups of two methylesters (COOCH_3), four equivalent methine (4 CH), two equivalent quaternary carbons (2 QC) of benzene nucleus and two equivalent carbonyl groups (2 CO) of the two ester functions appeared as single line at $\delta 53.38$, 129.52, 133.88 and 166.24 respectively. The compound isolated from the plant was found to be identical with the synthetic dimethylterephthalate in all respects (same R_f values, Co-TLC, mixed mp, superimposable IR), which gave an unambiguous proof for the structure. This is the first report of C-13, NMR of dimethylterephthalate Fig. 1.

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