2-(2-IMINOACETIC ACID)-3-(2H)-BENZOFURANONE: A NEW METABOLITE FROM SHOREA ROBUSTA SEEDS

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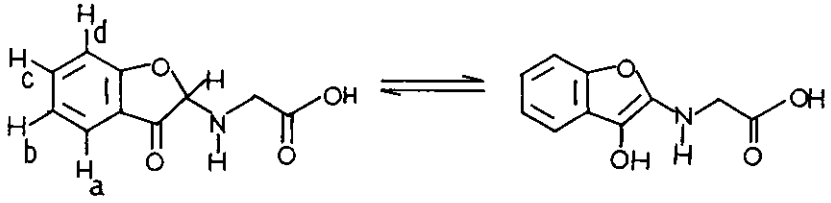
Abstract - A new metabolite, 2-(2-Iminoacetic acid)-3-(2H)-Benzofuranone has been isolated from the ethyl acetate extract of the defatted SHOREA ROBUSTA seeds. Its structure has been established using spectroscopic methods and by synthesis of its dimethyl derivative.

In the course of a search for toxin (s) reported [1] to be present in SHOREA ROBUSTA seeds, family Dipterocarpacea, which have ~62 lakh tonnes potential per annum in India, we have isolated a new metabolite together with gallic and ellagic acid. We wish to report the structure elucidation of the new metabolite (1) on the basis of spectroscopical evidences.



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The ethyl acetate extract of the defatted seeds was chromatographed on silica gel in a stepwise manner, fraction eluted with chloroform containing 2% methanol gave (1) as brownish-yellow solid: m.p. >340°decomp. The UV absorptions of the methanol solution at 288 nm, 255 and 222 suggested the presence of a conjugated carbonyl system. Its mass spectrum suggested M^+ at m/e 207 from which the composition was arrived at $C_{10}H_9NO_4$ as the presence of nitrogen was also indicated by qualitative analysis. The main fragmentations observed were 161 (63.6%), 148 (67.3%), 133 (32.7%), 120 (base peak), 92 (67.3%) and 65 (45.5%). Infrared spectrum as KBr pallet showed nitrogen to be present probably in the form of imino group, as a sharp band at 3390 cm^{-1} was observed in the =NH streching region, which looks to be present as a part of linear chain as can be seen from mass spectrum (Fig. 1) and (Fig. 2). Intense absorption at

1705 cm^{-1} (carbonyl streching) along with broad band in-O-H streching region (3400 - 2800 cm^{-1}) accounted for two oxygens in the form of a carboxylic group. Also absorption at 755 cm^{-1} as sharp band indicated the presence of 1, 2 - di - substituted benzene ring. Nuclear magnetic resonance spectrum in deutroacetone at 100 MHz showed a singlet at δ 9.40 along with a broad hump ranging from δ 4.0 - 2.8, both corresponding to 1H and exchangeable with D_2O, which can be assigned to -COOH and = NH groups. Besides these, it showed a well resolved 4H multiplet for aromatic protons, corresponding to ABCD pattern of benzene ring - δ 7.50 ($1H_a$, dd, J_{ab} = 10 Hz & J_{ac} = 2 Hz), 7.30 ($1H_c$, distorted t, $J_{cb} = J_{cd}$ = 10 Hz & J_{ca} = 2Hz), 7.00 ($1H_d$, dd, J_{dc} = 10 Hz & J_{db} = 2 Hz) and 6.95 ($1H_b$, multiplet) - also a 2H singlet at 3.08 was observed, indicating the presence of a methylene group. The multiplicity and chemical shift of the four aromatic protons gave the hint of the presence of a 1,2-substituted ortho-oxygenated-carbonyl benzene system, which may account for the rest two oxygens. Support to the presence of such group can be seen from the observation of base peak in mass spectrum at m/e 120 (Fig. 1) and UV λmax at 255 nm. On the basis of above observations, the structure of the metabolite can be assumed as (1), which looks to be in equilibrium with its enolic form.

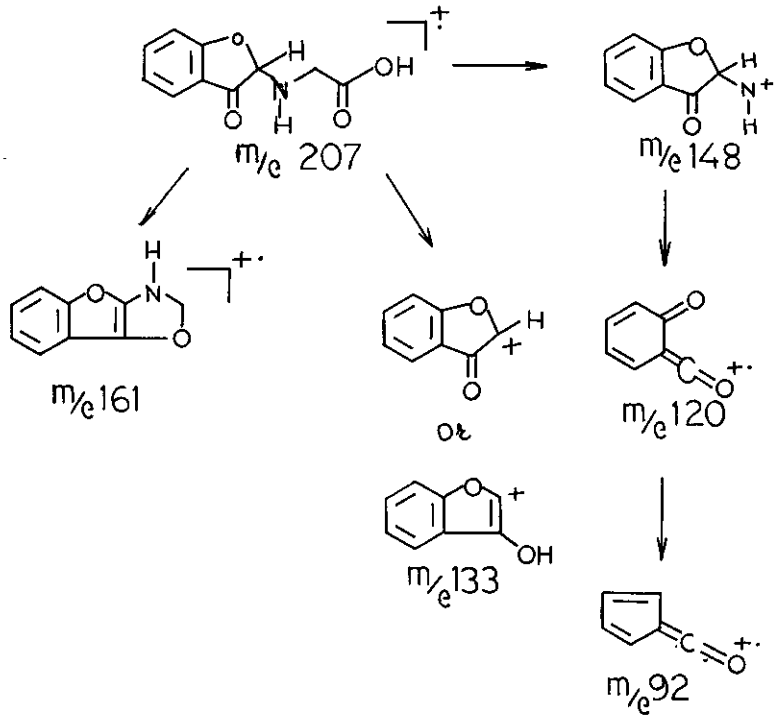

FIG. 1

Methylation of (1) with methyl iodide in presence of anhydrous potassium carbonate by refluxing in acetone for 3-4 hr gave a dimethyled derivative as seen from its NMR spectrum, which showed two 3H singlets at δ 3.40 and 3.15 along with the original spectrum. Its mass spectrum showed M^+ at m/e 235 with base peak at m/e 134 (Fig. 2). UV absorptions in methanol showed λmax at 286 nm, 257 and 237. Absence of free carboxylic acid can be inferred from the IR spectrum as the hump in O-H streching region was missing.

Confirmation to the structure (1) of the metabolite has been provided by the synthesis of its dimethyl derivative. It involves condensation of 2-bromo-3(2H)-benzofuranone[2] with methyl glycinate hydrochloride[3] in chloroform in presence of triethylamine as base. Methylation of the resulting product under the similar conditions as has been used for natural compound provided a mixture from which isolation using preparative TLC gave the desired compound, identical Co-TLC and UV spectrum to the dimethyl derivative of natural sample (1).

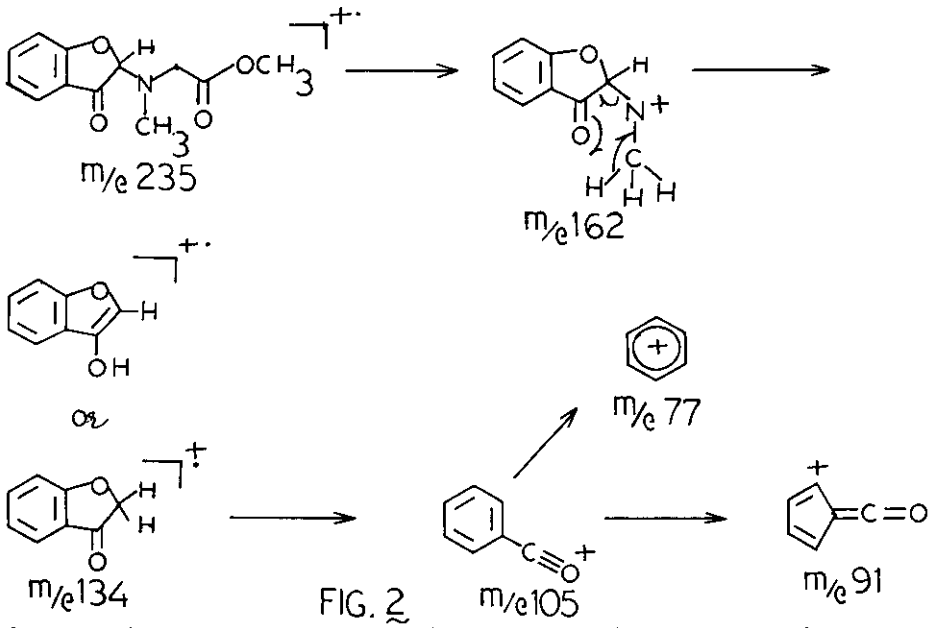

FIG. 2

Isolation of compound (1) is interested as very few O-heterocyclic derivatives of amino acids are known to occur. Metabolite (1) looks to have biosynthesised using acetate-malonate pathway via polyketide intermediate involving in between condensation with requisite amino acid, followed by cyclization.

Acknowledgments.

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References.

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