

GC-MS STUDIES OF NON-SAPONIFIABLE PRINCIPLES OF THE SEED COATS OF *ERYTHRINA SUBEROSA* ROXB

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ERYTHRINA SUBEROSA Roxb^{1,2} (N. O. Leguminosae) is a medium-sized tree with deeply cracked corky bark. The plant is known as 'Pangra', from the plains of Punjab, its bark is reported to have important medicinal values³ and its leaves are useful for curing malignancy⁴.

The dried and powdered seed coats of *E. suberosa* were extracted with petroleum ether (40–60°) and the extract when concentrated yielded a deposit whose TLC showed it to be homogeneous; it responded to positive tests for steroids^{5–9}, could not be crystallized and was obtained in white amorphous powder, m.p. 155–56°. Its GC-MS analysis revealed that it was an azeotropic mixture of β -sitosterol (37.5%), campesterol (10.2%) and stigmasterol (22.5%).

Its mass spectroscopic examination showed the presence of three molecular ion peaks corresponding to $m/e = 414, 412$ and 400 indicating that it is not a single compound but a mixture of three compounds¹⁰ viz β -sitosterol ($M^+ = 414$), stigmasterol ($M_2^+ = 412$) and campesterol ($M_3^+ = 400$). Other significant peaks observed were at $m/e = 399, 396, 381, 329, 303, 273$ and $255, m/e = 394, 379, 365, 351$ and 300 and $m/e = 385, 382, 315$ and 301 which could be confirmed fragmentation ions of β -sitosterol, stigmasterol and campesterol respectively.

Its GLC analysis was done taking cholestane as reference with N_2 as carrier gas at 110 ml/min. GLC analysis showed three peaks having relative retention time 2.60 (campesterol), 3.02 (β -sitosterol) and 2.58 (stigmasterol). GLC analysis confirmed that it was a mixture β -sitosterol (37.5%), campesterol (40.2%) and stigmasterol (22.2%).

A survey of chemical literature revealed that whenever β -sitosterol, campesterol and stigmasterol are present together in a plant they always form a mixture which is unresolvable by column or thin layer chromatography.

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STUDIES ON THE CHLORINATION OF PHTHALIDE. PREPARATION OF 2-CHLOROMETHYL AND 2,2-DICHLOROMETHYLBENZOYL CHLORIDE

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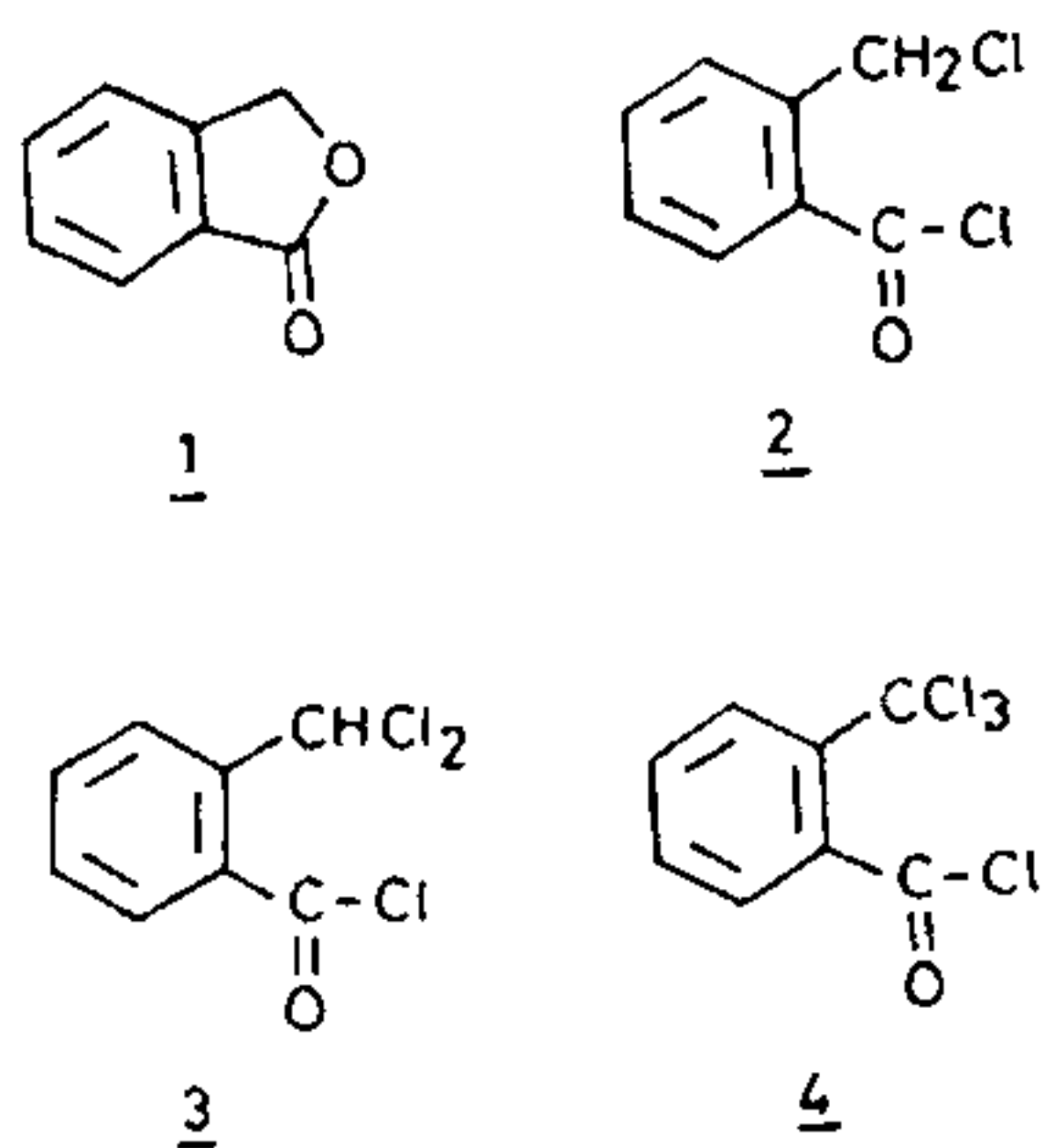
AS a part of a study of the ring opening reactions of phthalide, 1, its reaction was studied with various chlorinating agents. It has been reported¹ that 1 can be converted to chloro derivatives 2, 3 and 4 by the action of reagents such as phosphorus pentachloride, usually resulting in mixtures. No convenient laboratory preparation to obtain these compounds selectively is available. The present paper deals with the reaction conditions for the conversion of 1 to 2 and 3.

Our results show that at 55–60°C, the reaction of solid phosphorus pentachloride with 1 as reported was not complete even in 8 hr and a mixture of all the three chlorides was obtained. When the reaction was carried out in chlorobenzene solution at $140 \pm 5^\circ\text{C}$ for 4.5 hr 3 was obtained in 91% yield along with about 1% of 4. The composition was estimated by converting the crude reaction product into the anilide and analyzing the anilide mixture by HPLC and by the isolation of

the components by TLC. The above are the optimum conditions for the selective formation of 3. When the reaction was repeated at $155 \pm 5^\circ\text{C}$ for 6 hr, 3 and 4 were obtained in the ratio 58:42, analyzed as the anilides. The use of chlorobenzene as solvent is essential for selectivity.

The chloromethyl derivative 2 could not be obtained from 1 by the use of phosphorus pentachloride. An alternate route, namely, the use of phthaloyl chloride and anhydrous zinc chloride was followed for this preparation. The use of zinc chloride-phthaloyl chloride has been reported² for the conversion of maleic anhydride to fumaroyl chloride.

Phthaloyl chloride is commercially available or it can be easily prepared, as was done in our experiments, from phthalic anhydride and phosphorus pentachloride. By this technique 1 could be converted to 2 in 60% yield uncontaminated by 3 or 4.



Thionyl chloride-zinc chloride has been used³ to convert γ -butyrolactone to 4-chlorobutyryl chloride. However the reagent failed to open 1.

1. 2-chloromethylbenzoyl chloride (2)

Anhydrous zinc chloride (0.5 g) was heated to its melting point and evacuated for 30 min⁴. The flask containing zinc chloride was set up for refluxing protected from atmospheric moisture and 45 g of freshly distilled phthaloyl chloride and 27 g of phthalide were added. The mixture was heated for 3.5 hr maintaining the inside temperature at $130 \pm 10^\circ\text{C}$. Distillation of the reaction product yielded a fraction b.pt. $149^\circ\text{--}151^\circ\text{C}/20$ mm Hg (Lit¹ b.pt. $135^\circ\text{C}/12$ mm Hg). Yield: 25 g (66%), IR (film) 1770, 1740 cm^{-1} , NMR (δ , CDCl_3): 4.89, singlet, 2H and

7.40–8.29, multiplet, 4H. Mass spectrum confirmed the presence of two chlorine atoms.

2. 2,2'-Dichloromethylbenzoyl chloride (3)

Phthalide (13.4 g, 0.1 M) was warmed to its melting point and phosphorus pentachloride (59 g, 0.28 M) was added in instalments such that the reaction was not vigorous and occasional cooling was done to control the reaction. Dry chlorobenzene (100 ml) was then added and the mixture was refluxed at $140 \pm 5^\circ\text{C}$ (bath temperature) for 4.5 hr cooled and phosphorus oxychloride and chlorobenzene removed under vacuum. Distillation of the thick brown liquid yielded a colourless liquid b.pt. $135^\circ\text{--}7^\circ\text{C}/15$ mm Hg (Lit.¹ $155\text{--}7^\circ\text{C}/28$ mm Hg). Yield: 20 g (90%), IR (film): 1780, 1740 cm^{-1} , NMR (δ , CDCl_3): 7.25–8.26 multiplet, UV (CHCl_3 , nm): 242, 279, MS (70 eV): M^+ 222 isotope peaks conforming to three chlorine atoms.

The anilide m.pt. 127°C (Lit.¹ 129°C) gave the following spectral data: IR (KBr) 1660, 1645 cm^{-1} , MS (70 eV) M^+ 279, with isotope peaks confirming the presence of two chlorine atoms. HPLC of the mixed anilide showed the presence of 3 and 4 in the ratio of 99:1.

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4. In these studies it was found that zinc chloride pretreated in this manner gave better results than fresh zinc chloride.