Short Communication

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SYNTHESIS OF KARANJIN, NATURALLY OCCURRING FURANOFLAVONE

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Karanjin was isolated from *Tephrosia purpurea* and formulated as a 3-methoxy-8-phenylfuro [2, 3-h] benzopyran-6-one (**7**) on the basis of spectral data (Sinha *et al* 1982) but no synthetic proof was provided. The chalcone (**5**) was obtained by the aldol condensation of 5-acetyl-4-hydroxybenzofuran (**4**) with benzaldehyde. β-Resacetophenone (Clarke 1955) (**1**) when refluxed with allyl bromide in presence of potassium carbonate and acetone yielded 4-O-allylresacetophenone (Rangaswarnis *et al 1954*) (**2**) which on Claisen migration gave 3-C-allylrescetophenone (Baker and Lothin 1935) (**3**). This was subjected to O_sO_4/KIO_4 oxidation followed by orthophosphoric acid cyclizatin to (Naik *et al* 1975) (**4**). Peroxide treatment of (**5**) gave the flavone (**6**) which on selective methylation afforded karanjin (**7**).

Melting points were determined on an electrothermal melting point apparatus (Gallenkamp) and are uncorrected. IR spectra were recorded on KBr discs on a Pye-Unicam SP$_3$-300IR spectrophotometer (ν_{max} in cm^{-1}), ^{1}H-NMR spectra were recorded on a Perkin-Elmer R-32 (90MHz) spectrophotometer in $CDCl_3$ with tetra methylsilane as an internal standard (chemical shifts in δ values) and UV spectra were recorded on LKB 4053 Ultrospeck spectrophotometer in methanol (λ_{max} in nm). Thin layer chromatography was performed using silica gel GF$_{254}$. Mass spectra were recorded on VG 7070E anlytical mass spectrometer.

*4-0-Allylresacetophenone(**2**).* β-Resacetophenone (Clarke 1955), **1**(15 g) in acetone (75 ml) was refluxed with allyl bromide (12.5 g) and anhydrous potassium carbonate (60 g) for 6 h. Inorganic salts were filtered off and washed with acetone. Acetone was removed by distillation. The residue was taken up in ether and extracted with 5% aq. sodium carbonate solution and then with 5% sodium hydroxide solution. Sodium hydroxide extract was acidified and again extracted with ether **2** (100 ml), dried over anhydrous sodium sulphate and concentrated when a dark colored oil (16 ml) was obtained; b.p. 156-57°C (9 mm) (Rangaswarnis *et al 1954*).

*3-C-Allylresacetophenone(**3**).* The above 4-O-allylresacetophenone (Rangaswarnis *et al* 1954), **2** (4 g) was heated in an oil-bath cautiously. Rearrangement occurred at 180°C with evolution of heat and the test tube was raised for a few min. Then the temperature was maintained at 210°C-215°C for 2 h, when a pink colored solid was obtained. The crude mixture was fractionated using column chromatography over silica gel and benzene as eluent. Earlier fractions gave some oil and then pure 3-C-allylrescetophenone was obtained as colorless needles (1.3 g); m.p. 132-133°C (Baker and Lothin 1935).

*5-Acetyl-4-hydroxybenzofuran(**4**).* 3-C-Allylresacetophenone (Baker and Lothin 1935), **3** (500 mg) was dissolved in ethyl acetate (200 ml); an equal volume of water and osmium tetraoxide (100 mg) was added. The mixture was stirred on a magnetic stirrer for 1.5 h, during which period potassium periodate (3 g) was added in small quantities and the mixture was stirred for further 2 h. The ethyl acetate layer was separated and the aq. solution was further extracted with ethyl acetate (2x50 ml). The combined ethyl acetate extract was washed well with water, dried over anhydrous sodium sulphate and the solvent was distilled off. The residue obtained as dark colored oil was heated on a water-bath with orthophosphoric acid (20 ml) for 20 min and then poured over crushed ice. The solid that separated was taken up in ether and the ether solution was washed successively with 5% sodium carbonate solution, water and dried (over anhydrous sodium sulphate). The solvent was distilled off and the residue was taken up in benzene and passed through a column of neutral alumina when colourless flakes (230 mg) were obtained; mp 85°C (Naik *et al* 1975; mp 86°C); (M$^+$, 176) [Anal. found(%): C, 67.92; H, 4.91; Calc(%) for $C_{10}H_8O_3$: C, 68.18; H, 4.54]; UV; 235, 275, 325 nm; IR; 3440, 1630, 1585, 1500, 1440, 375 cm^{-1}, ^{1}H-NMR; δ 2.45 (s, 3H, -COCH$_3$), 6.98 (d, 1H, J=2 Hz, H-4$^{\prime}$), 7.05 (d, 1H, J=9 Hz, H-5), 7.55 (d, 1H, J=2 Hz, H-5$^{\prime}$), 7.65 (d, 1H, J=9 Hz, H-6), 13.90 (s, 1H, -OH).

*4-Hydroxybenzofuran-5-chalcone (**5**).* A mixture of **4** (200 mg) and benzaldehyde (110 mg) in ethanolic solution of potassium hydroxide (50%, 15 ml) was kept at room temperature for about 75 h. The reaction mixture was diluted with ice-cold water, acidified with cold dil. hydrochloric acid and extracted with ether. The ether layer was washed with water, dried over anhydrous sodium sulphate and evaporated to dryness. It crystallized from benzene-petroleum spirit (b.p 40-60°C) as yellow needles (70 mg), m.p 172°C; (M$^+$, 264); R$_f$ 0.61 (benzene-ethylacetate; 15:1), UV; 250, 275, 345, IR; 3440, 2810, 2760, 2110, 1645, 1605, 1575, 1470, 1420, 1360,

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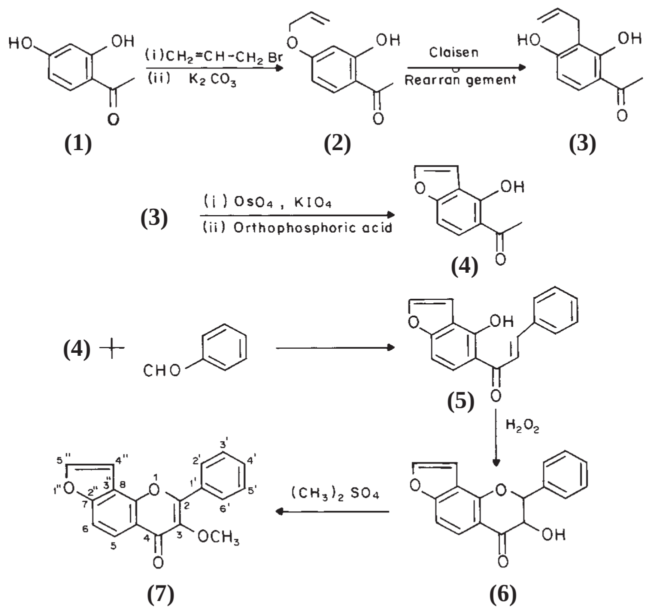

Scheme 1

^{1}H-NMR; 6.81 (d, 1H, J=9Hz, H-5$^{/}$), 7.14 (d, 1H, J=2Hz, H-4$^{//}$), 7.45 (d, 1H, J=9Hz, H-α), 7.55 (s, 5H, aromatic protons), 7.73 (d, 1H, J=2Hz, H-5$^{//}$), 7.89 (d, 1H, J=9Hz, H-6$^{/}$), 8.00 (d, 1H, J=2Hz, H- β), 12.01 (s, 1H, -OH); [Found: C, 77.3; H, 4.5, $C_{17}H_{12}O_3$ requires: C, 77.7; H, 4.8%].

*7-Hydroxy-8-phenylfuro [2, 3-h]benzopyran-6-one (**6**).* To the above chalcone **5** (1.05 g) in pyridine (25 ml) and sodium hydroxide (20%, 40 ml) kept at 60-70°C, hydrogen peroxide (30%, 60 ml) was added with stirring during 15 min. The reaction mixture was acidified within 20 min. and the solid that separated was filtered. The solid was recrystallized methanol as yellow needles (0.51 g), m.p 182°C; (M+, 278); R_f,0.54 (benzene), UV; 225, 274, 325, IR; 3520, 2910, 2875, 1645, 1600, 1510, 1472, 1375, 1365; ^{1}H-NMR; 6.78 (d, 1H, J=2Hz, H-4$^{//}$), 7.51 (s, 5H, aromatic protons), 7.82 (d, 1H, J=2Hz, H-5$^{//}$), 7.92 (d, 1H, J=9Hz, H-5$^{//}$), 12.75 (s, 1H, -OH); [Found: C, 73, 4; H, 3.6, $C_{17}H_{10}O_4$ requires: C, 73.6; H, 3.2%].

*7-Methoxy-8-phenylfuro [2,3-h]benzopyran-6-one (**7**, Karanjin).* A mixture of 3-hydroxyfurano (2$^{//}$, 3$^{//}$: **7**, **8**) flavone (**6**, 1.40 g), dimethyl sulphate (0.228 g) and anhydrous potassium carbonate (10 g) in acetone (50 ml) was refluxed for 2 h. Acetone was removed by distillation, water was added to the residue and was extracted with ether. The ether layer was washed with water, dried over anhydrous sodium sulphate and evaporated to dryness. The product was purified by preparative thin layer chromatography over silica gel GF_{254} using methanol-chloroform (10: 1) as developing solvent. It was crystallized from methanol to give yellow crystals (0.68 g), m.p 159°C (*Sinha et al* 1982; m.p 158-159°C); R_f 0.61 (methanol-chloroform; 10: 1), (M^+, 292), UV; 232, 264, 385, IR, 1645, 1605, 1590, 1470, 1372, 1365, 1147, ^{1}H-NMR, 3.95 (s, 3H, -OCH_3), 6.75 (d, 1H, J=9Hz, H-6) 7.15 (d, 1H, J=2Hz, H-4$^{//}$), 7.53 (s, 5H, aromatic protons), 7.85 (d, 1H, J=2Hz, H-5$^{//}$), 7.95 (d, 1H, J=Hz, H-5); [Found: C, 74.0; H, 4.1. $C_{18}H_{12}O_4$ requires; C, 74.3, 4.5%].

Key words: Synthesis, Karanjin, Furanoflavone.

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