phenylalanine, proline, serine, threonine and tyrosine was detected in measurable quantities. Valine although present in appreciable quantity in the tasar silk fibre of *A. mylitta*, was detected only in traces in the fibres of *Attacus atalus* and *Philosamia ricini*. The sulphur containing amino acids, methionine and cystine were conspicuous by their absence in all the three fibres. This is in line with the previous findings in the spider silk[12]. On the contrary, cystine was detected in *B. mori* in measurable amounts in both the protein fractions of the silk *i.e.*, silk, sericin and fibroin[13]. Also Gamo *et al.*[14], demonstrated the presence of SH groups in the *B. mori* silk fractions.

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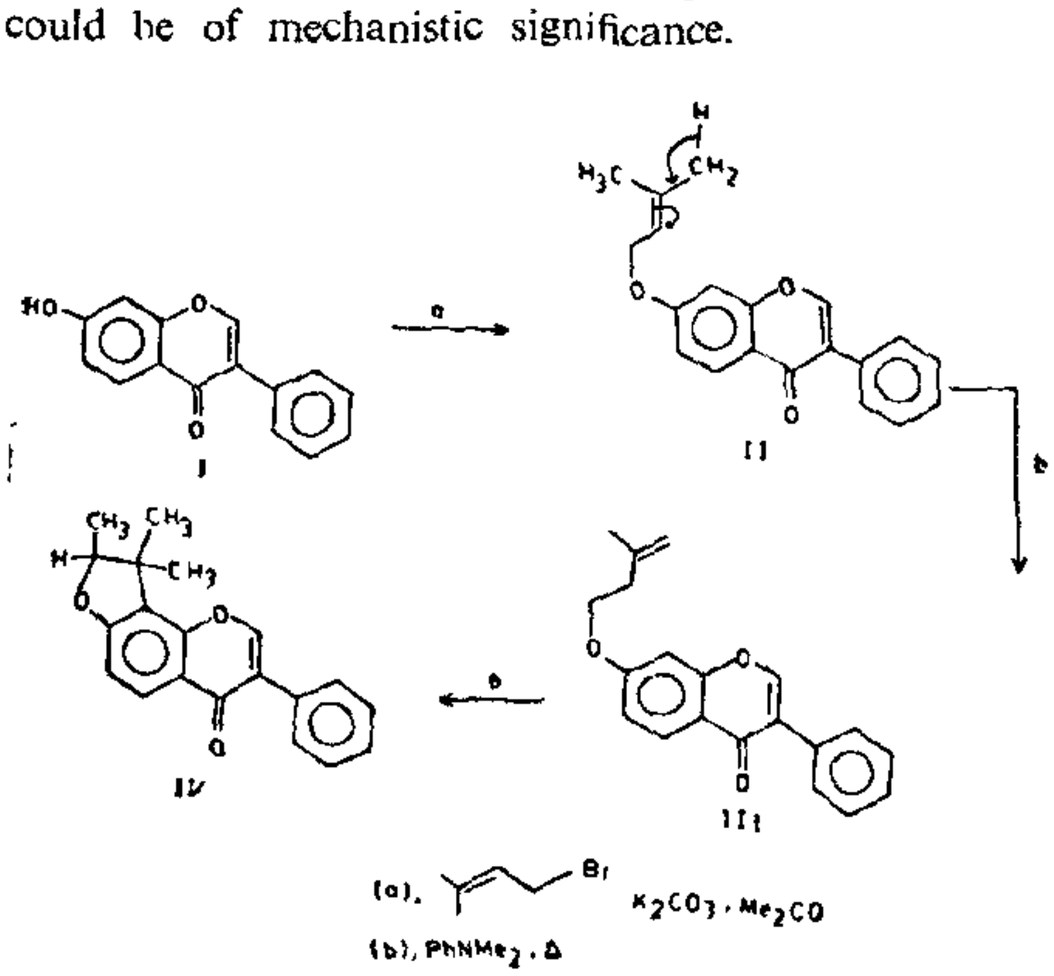
A NOVEL OBSERVATION IN THE CLAISEN REARRANGEMENT OF 7-PRENYLOXYISOFLAVONE

IN continuation of our work on the Claisen reararngement of cinnamyl and prenyl ethers of complex polyphenols[1–4], the rearrangement of 7-prenyloxyisoflavone in refluxing *N*, *N*-dimethyl aniline was studied. As the results obtained were different from the earlier reports, our observations are reported here.

7-Prenyloxyisoflavone (II) prepared from 7-hydroxyisoflavone[5] (I) by refluxing, with prenyl bromide in acetone and potassium carbonate was crystallised from benzene-light petroleum mixture as colourless crystals, m..p 155–56° C; λ_{max} (MeOH) 248 and 300 nm (log ϵ 4·53 and 4·21 respectively) (Found: C, 78·0; H, 6·1. $C_{20}H_{18}O_3$ requires C, 78·4; H, 5·9%); 60MHz NMR ($CDCl_3$): δ 1·75 [2s, 6H, $=C(CH_3)_2$], 4·40 (d, J = 7Hz, 2H, $-OCH_2-$), 5·40–5·48 (m, 1H, $=CH-$) 6·78, 6·81 (2d, J_o = 9Hz, J_m = 2·5Hz, 1H, H–6), 6·87 (d, J_m = 2·5 Hz, 1H, H–8), 7·35–7·41 (m, 5H, $-C_6H_5$), 7·81 (s, 1H, H–2) and 8·10 ppm (d, J_o = 9Hz, 1H, H–5).

The above prenyloxyisoflavone (II) when refluxed with *N*, *N*-dimethylaniline for 3 h gave a product in almost quantitative yield, insoluble in aq. Na_2CO_3; m.p. 126–28° C. The NMR spectrum showed the resonance signals of all the three aromatic hydrogens of ring A as in the parent ether (II). However, the prenyloxy unit of II was found in the form of 3-methyl-3-butenyloxy form, showing two triplets at δ 2·48 and 4·12, a singlet of an unsaturated methyl group at δ 1·75 and a multiplet of two olefinic hydrogens at δ 5·27. Hence, the structure of this product must be 7- (3-methyl-3-butenyloxy) isoflavone (III) and it represents an allylic arearrangement of the hydrogen atom of the prenyloxy group as shown in II. Such a rearrangement has not been reported earlier and could be of mechanistic significance.



When III was heated for a longer period, it gave two products. The minor compound was found to be simple 7-hydroxyisoflavone (I) and the major compound crystallised from ethyl acetate-light petroleum mixture to give 4″, 4″, 5″-trimethyl-4″, 5″-dihydrofuro (2″, 3″: 7, 8) isoflavone (IV), m.p. 136–137° C; n.m.r. spectrum: δ 1·27, 1·51 [6H, s, $>C(CH_3)_2$], 1·37 (3H, d, J = 6·5Hz, CH_3-CH-O), 4·51 (1H, q, J = 6·50Hz, $-O-CH-CH_3$), 6·77 (H, d, J = 9Hz, *H*–6), 7·23–7·53 (5H, m, $-C_6H_5$), 7·87 (1H, s, *H*–2) and 8·10 ppm (1H, d, J = 9Hz, *H*–5).

The formation of IV from III does not seem to be a case of direct Claisen rearrangement. It appears that III again rearranges to II which in turn gives IV as a *normal rearrangement product followed by cyclisation* with the *ortho* phenolic group.

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SYNTHESIS OF *2-p-CHLOROPHENOXYMETHYLCHROMONE*

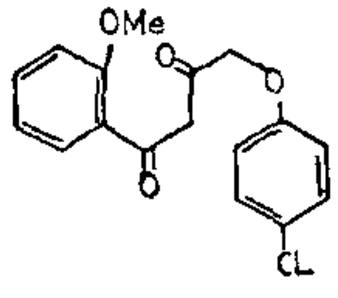
SEVERAL synthetic approaches have been tried for the chromanochromone skeleton (III), in view of interesting pesticidal properties of the rotenoids[1]. A simple route to phenoxymethylchromones (II) is described; however the initial attempts at its conversion to the parent tetracyclic system (III) have not been successful.

A Claisen-Schmidt condensation of *o*-methoxyacetophenone and ethyl *p*-chlorophenoxyacetate occurred in the presence of potassium tert. butoxide leading to the *β*-diketone (I). Spectral evidence indicated that the diketone exists in the enol form (I *a*): i.r. 3040, 1617 cm^{-1} (broad, intense) characteristic for enol form of *β*-diketone[2,3]; n.m.r. ($CDCl_3$) δ 3·78 (3H, s, $-OMe$), 4·67 (2H, s, $-CH_2OAr$), 6·8–8·1 (9H, m, 8 arom. + 1 conj. olefinic), 16 (1H, br. s, enol OH)[4] (the methoxyl and the methylene peaks had shoulders and there was a small absorption integrating 0·2H at 4·2 δ probably arising due to tautomers).

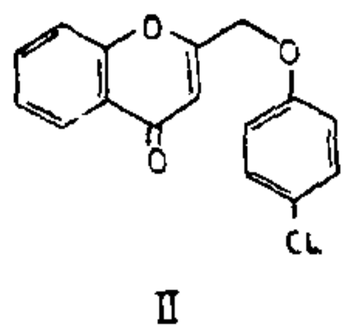
Treatment of the diketone (I) with refluxing hydriodic acid led to demethylation and cyclisation to 2-*p*-chlorophenoxymethylchromone (II); i.r. 1655 cm^{-1} (*α*, *β*-*α'*, *β'*-unsaturated ketone)[3] and absence of hydroxyl absorption; n.m.r. ($CDCl_3$) δ 4·98 (2H, s, OCH_2Ar), 6·59 (1H, s, 3H of pyrone), 6·9–8·4 (8H, m, arom.)[4]

Experimental

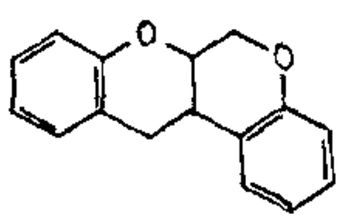
1-o-*Methoxyphenyl*-1, 3 4-p-*chlorophenoxybutan*-1,3-*dione* (*I*): A mixture of *o*-methoxyacetophenone (3·7 g), ethyl *p*-chlorophenoxyacetate (5·4 g) and potassium tert butoxide (from 1 g of potassium and 30 ml tert. butanol) was stirred under inert anhydrous *conditions at room temperature for 30 min.* The reaction mixture was acidified to Congo red with 3N hydrochloric acid, and the butanol removed under reduced pressure. Ether was added, the aqueous phase separated and the ethereal solution washed with sodium bicarbonate solution and brine. After drying (Na_2SO_4) and removal of solvent, the ether solution yielded the diketone (6 g), crystallised from aqueous acetone, m.p. 106°. It gave an intense blood-red colouration with alcoholic ferric chloride. Found: C, 63·79; H, 4·53; Cl, 11·25%. $C_{17}H_{15}O_4Cl$ requires C, 64·04; H, 4·74; Cl, 11·13%.



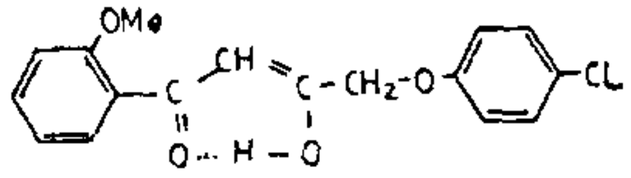
I



II



III



Ia

2-p-*Chlorophenoxymethylchromone* (*II*): The diketone (I) (2·2 g) and purified hydriodic acid[5] (75 ml) were refluxed at 130° for 40 min. The reaction mixture was cooled and diluted with water when a dark sticky solid precipitated. It was taken up in warm pyridine and a little water added when a gummy material was formed. To the clear warm filtrate were again added a few drops of water, and the sticky material formed discarded[6]. The clear hot solution was chilled when the chromone (II) precipitated as a fine yellow solid (1·3 g). It crystallised from aqueous ethanol, m.p. 132°. Found: C, 66·84; H, 4·03; Cl, 12·52%. $C_{16}H_{11}O_3Cl$ requires C, 67·04; H, 3·87; Cl, 12·37%.

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