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A NOVEL PHOTO-REARRANGEMENT OF LATIFOLIN

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The 3,3-diphenyl allyl skeleton (Ia) of latifolin, a recently discovered[1] member of the neoflavonoids, shows some interesting reactions[2] and rearrangements[3]. In this paper we describe a novel photochemical transformation of this molecule.

Irradiation of a 5% solution of latifolin dimethyl ether (Ib) (the free phenol itself gave a complex mixture) in benzene or in hexane in pyrex cells using a Philips BIOSOLS 200 watts high pressure Hg-lamp, at room temperature slowly produced a new compound in excellent yield (90%). Even strong sunlight filtered through pyrex was found to be quite effective, complete conversion requiring 5 or 6 days. The same compound was produced in alcohol or acetone solution but there were some side reactions necessitating chromatographic purification. Addition of sensitisers like benzophenone or cinchonine did not in any way affect the course of the reaction. Irradiation of the powdered solid however did not produce any change.

The new product crystallised from methanol as colourless rhombs, m.p. 100-101° (Found: C, 73.0; H, 7.4; $-OCH_3$, 39.7%; $C_{15}H_{10}(OCH_3)_4$ requires: C, 72.6; H, 7.0%; $-OCH_3$, 39.5%), λ_{max}^{EtOH} 292 mμ (3.46), Mol. wt. 314 (mass-spectral). Its IR spectrum showed absence of unsaturation and this was confirmed by its stability towards Lemieux-Rudloff reagent[4]. The compound was thermally stable as heating upto 200° did not produce any change. Its sensitivity towards strong acids was indicated by an immediate violet colour with hydrobromic acid in acetic acid. Under the same conditions (Ib) did not give any

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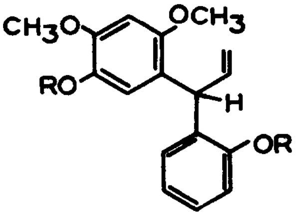
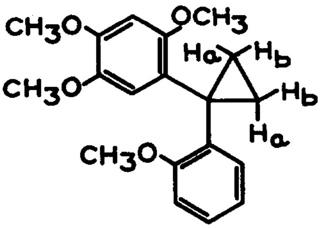
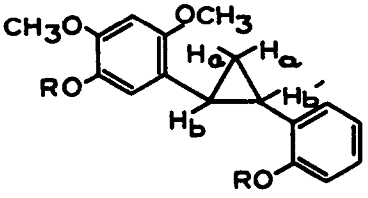
colour. Its analysis and mol. wt. indicated that it is isomeric with the starting substance and two structures (II) and (IIIa) could account for this data.



Ia, R= H .
b, R= CH_3 .
c, R= C_2H_5 .



II

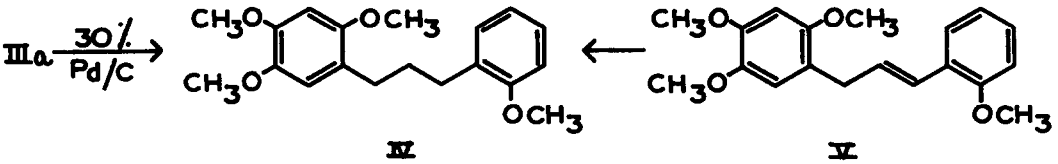


IIIa, R= CH_3 .
b, R= C_2H_5 .

The 60 Mc NMR spectrum of the compound in CCl_4 showed, besides aromatic and methoxyl protons, two groups of alicyclic protons at around τ8.7 (2P, irregular triplet) and around τ7.6 (2P, irregular triplet). The absence of vinylic protons confirmed the lack of unsaturation. However, the considerable difference (1.1 ppm) in the chemical shift of these two groups of protons was not in favour of structure (II). Although there are two groups of protons (Ha and Hb) in (II) their chemical shifts should not differ by more than 0.2 ppm[5]. This large difference in the chemical shift of these protons was more in accordance with structure (IIIa). The absorption at τ8.7 is due to the methylene protons (Ha) in (IIIa), its slight down field position is possibly due to the deshielding effect of the aryl groups. The absorption centered around τ7.6 is due to the benzylic protons Hb and Hb' in (IIIa).

Its 100 Mc NMR spectrum taken in C_6D_6 showed clearly the Hb and Hb' (IIIa) protons as a well resolved multiplet (5 lines) centered at τ7.6. Moreover in double resonance experiments, by irradiating the methylene protons at τ8.7 this multiplet collapses to a doublet (J$\approx$1.5 cps) clearly showing that the protons Hb and Hb' are non equivalent. The small coupling constant of these two protons is indicative of the trans stereochemistry of (IIIa).

Further confirmation of structure (IIIa) for this photoisomer was provided by hydrogenation experiments in ethanol (20 lb. p.s.i., 30% Pd/c) which yielded (IV) slowly. After chromatography on basic alumina and elution with a mixture of petroleum ether and benzene (1:1), it crystallised from methanol as colourless needles, m.p.71-72°, λ_{max}^{MeOH} 278 mμ (3.18) and 288 mμ (3.17) (Found: C, 72.1; H, 7.9; $C_{19}H_{24}O_4$ requires: C, 72.1; H, 7.6%). Its NMR spectrum in CCl_4 showed two multiplets centered around τ8.2 (2P) and around τ7.4(4P). The absence of a methyl peak in this spectrum clearly excludes structure (II) for the photoisomer. The structure of the hydrogenation product was finally confirmed by direct comparison with an authentic specimen prepared by hydrogenation of the corresponding benzyl styrene[6] (V).



It is well known that olefinic compounds undergo cyclo-addition to form 4-membered derivatives on UV irradiation. The formation of a cyclopropane derivative accompanied by a phenyl migration is rather novel and as far as we know has few parallels in literature. Hence the generality of this reaction was investigated with the help of a few suitable models. The diethyl ether of latifolin (Ic) also underwent similar photoisomerisation to give (IIIc) as colourless rhombs from methanol, m.p.86-7° (Found: C, 74.0; H, 8.0; $C_{21}H_{26}O_4$ requires C, 73.6; H, 7.6%); mol. wt. 342 (mass-spectral), λ_{max}^{EtOH} 290 mμ (3.58).

The intramolecular nature of this transformation was shown by the fact that no crossed products were found on irradiation of a mixture of the dimethyl and diethyl ethers of latifolin.

An isolated double bond is necessary for this isomerisation as neither dihydrolatifolin dimethyl ether nor isolatifolin dimethyl ether and the isomeric benzyl styrene (V) showed any transformation products under the same conditions of irradiation. Simple allyl compounds like o-methoxy or hydroxy allyl benzene and eugenol methyl ether also remained unaffected.

The present results obviously do not define the exact nature of the excited species or the detailed mechanism of this photorearrangement. Possibly it may involve excitation of the double bond to a diradical followed by phenyl migration to a more stable 1:3 radical and recombination of the new radical to cyclopropane ring. But the wave length employed is not sufficient to cause excitation of an isolated double bond directly. Probably the more substituted aryl group absorbs energy and by internal conversion produces an excited ground state which undergoes the rearrangement.

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