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PHOTOCHEMISTRY OF LATIFOLIN AND SOME RELATED COMPOUNDS

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Abstract- Latifolin (1),the major constituent of D.latifolia gave trans 1-(2,4-dimethoxy-3-hydroxyphenyl)-2-(2-hydroxyphenyl) cyclopropane as the sole photo di-π-methane rearrangement product. In contrast, its simpler analogues, 3-(2,4,5-trimethoxyphenyl)-3-phenyl prop-1-ene(3) and 3-(2,4-dimethoxyphenyl)-3-phenyl prop-1-ene(4),gave 1:1 mixture of cis and trans cyclopropanes. Dye-sensitized photooxidation of latifolin(1) and dihydrolatifolin (16) gave novel xanthan derivatives(15) and (17) involving a crucial step of photooxidative demethylation followed by cyclisation. Similar reaction of the closely related propane 19 gave, interestingly the benzofuran 20.The propene 22, lacking free hydroxyl or double bond, gave only the quinone 23 indicating that quinones are intermediates in the above oxidations. The allyl alcohol 24, having similar feature, undergoes oxidation to the corresponding aldehyde 26 and the benzophenone 28 but not to a quinone.

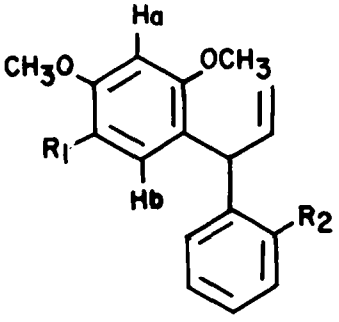
Latifolin (1), the major constituent of the heartwood of Dalbergia latifolia is an important neoflavonoid. Its dimethyl ether 2 was shown in a preliminary report[1] to undergo a facile photorearrangement, known under the general name of di-π-methane rearrangement[2,3]. We report here a detailed investigation of this rearrangement with latifolin itself and some of its simpler synthetic analogues. The isolation and characterisation of several novel photooxidation products of latifolin and some related compounds are also reported in this paper.

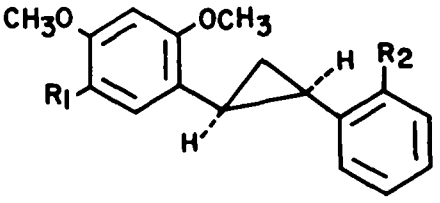
RESULTS AND DISCUSSION

Latifolin 1, on irradiation with UV-light filtered through pyrex gave a single photoproduct. Its IR spectrum showed a strong peak at 1031 cm^{-1} (cyclopropane) in addition to two hydroxyl peaks at 3500 and 3580 cm^{-1}.Its ^1H NMR spectrum exhibited two singlets at δ 4.01 and 4.10 equivalent to six protons of two methoxyl groups, in addition to two multiplets centred at δ 1.25 and 1.93 as expected of cyclopropanic protons. Its mass spectrum indicated that it is isomeric with latifolin itself. On the basis of these spectral data it was assigned the structure 1-(2,4-dimethoxy-3-hydroxyphenyl)-2-(2-hydroxyphenyl) cyclopropane (5). This was further confirmed when on methylation it gave the tetramethoxy compound 6 identical with the product reported earlier from the photorearrangement of latifolin dimethyl ether 2. The assignment of trans stereochemistry earlier[1] to 6 was based on spectroscopic grounds. Hence 5 also should have trans orientation.

Photoirradiation of the simpler analogue, 3-(2,4,5-trimethoxyphenyl)-3-

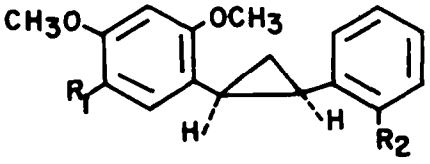
phenyl prop-1-ene (3), under the same conditions gave a mixture of two closely related cyclopropanic compounds (TLC) which could be separated by repeated column chromatography on alumina to a higher melting (93-94°) and a lower melting (69-71°) compounds. Since both had the same molecular weight (MS) they must be isomeric cis and trans cycloprepane compounds. The higher melting isomer was assigned the trans configuration 7 as the chemical shifts of the aromatic protons in the ^{1}H NMR spectrum of this compound were more deshielded than these of the corresponding protons of the lower melting isomer. Such effects have been observed earlier[5]. The lower melting isomer (m.p.69-71°) should therefore have the cis configuration. ^{1}H NMR spectrum of the reaction mixture taken before separation exhibited two sets of peaks for each type of protons. Comparison of the area under the peaks of aromatic protons at δ 6.18 and 6.20 to H_a and H_b of the cis isomer 8 and at δ 6.35 and 6.42 due to corresponding protons of the trans isomer 7 showed that the mixture consists of approximately equal amounts of cis and trans cyclopropanes.

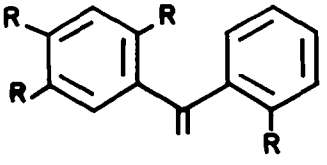




1, R_1=R_2=OH
2, R_1=R_2=OCH_3
3, R_1=OCH_3, R_2=H
4, R_1=R_2=H

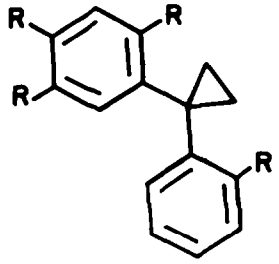
5, R_1=R_2=OH
6, R_1=R_2=OCH_3
7, R_1=OCH_3, R_2=H
9, R_1=R_2=H





8, R_1=OCH_3, R_2=H
10, R_1=R_2=H

11, R=H
12, R=OCH_3



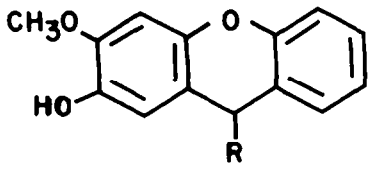
13, R=H
14, R=OCH_3

Similarly irradiation of 3-(2,4-dimethoxyphenyl)-3-phenyl prop-1-ene(4) yielded a viscous liquid which was found to be a mixture of two compounds having very close R_f values on $AgNO_3$ impregnated TLC plate. From ^1H NMR and MS spectra this also appeared to be a 1:1 mixture of cis and trans isomers of cyclopropane derivatives 9 and 10. It was not possible to separate this mixture.

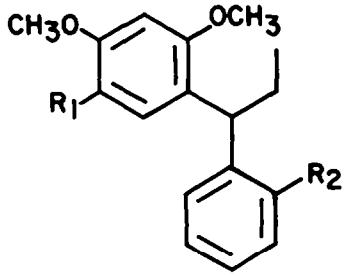
Thus, unlike latifolin (1) and its dimethyl ether 2 the di-π-methane rearrangement of simpler analogues gave both cis and trans isomers.

Attempted photochemical rearrangement of 1,1-diaryl cyclopropanes, as possible intermediates in di-π-methane rearrangement, examined with 1,1-diphenyl cyclopropane[6] (13) and its higher analogue 14 showed that such small ring systems do not undergo any change under these conditions. The required cyclopropanes 13 and 14 were synthesised from the corresponding 1,1-diaryl ethylenes 11 and 12 by Simmon-Smith reaction[8].

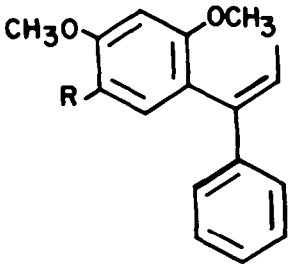
The Co-occurrence of latifolin[9] with a number of oxyheterocyclic and other oxidation products prompted us to explore the possibility of photochemical oxidation reactions of latifolin.



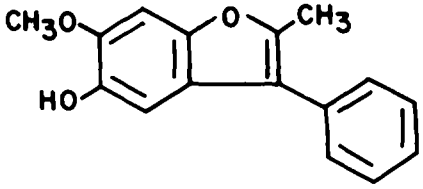
15, R=—CH=CH$_2$
17, R=—CH$_2$CH$_3$



16, R$_1$=R$_2$=OH
18, R$_1$=R$_2$=OCH$_3$
22, R$_1$=OH, R$_2$=H



19, R=OH
21, R=OCH$_3$



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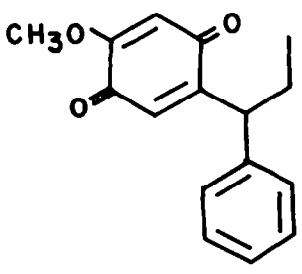
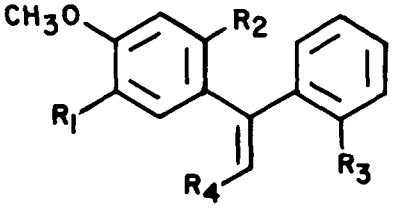


23

Latifolin (1) on photoirradiation in CCl_4 in the presence of rose-bengal gave a new product which could be characterised as the xanthan derivatives 15. ^1H NMR spectrum of this product displayed the presence of one methoxyl group at δ 3.8 and one D_2O exchangable proton at δ 5.25. The absence of the methoxyl peak at δ 3.9 and the OH peak at δ 5.7 originally present in the ^1H NMR spectrum of latifolin indicated that these sites were involved in the formation of the heterocyclic ring in 15. In a decoupling experiment, irradition of the multiplet centred at δ 5.9 caused the doublet of the proton centred at δ 4.45 collapse to a singlet and simultaneously the multiplet of $-CH=CH_2$ protons changed to a doublet. Similarly on irradiation of the doublet situation at δ 4.45, the multiplet of $-CH=CH_2$ proton collapsed to a double doublet thus showing that the ethylene side chain of 1 is intact in 15 and is not involved in the cyclisation. The mass spectrum of 15 exhibited a molecular ion peak at m/z 254 together with peaks at 253 (M^+-H) and at 227 ($M^+-C_2H_3$) corresponding to the loss of the benzylic proton and the side chain $-CH=CH_2$ respectively from the molecular ion. From these data the new product could be assigned the structure 3-methoxy-4-hydroxy-6-vinyl xanthan (15). Dihydrolatifolin (16) on dye-sensitized photooxidation also gave a new product 17 having similar structure. Comparison of the ^1H NMR spectrum of 16 and the photoproduct 17 revealed again the absence of one methoxyl and one hydroxyl group present in 16. Its mass spectrum which exhibited molecular ion peak at m/z 256 alongwith other peaks at 255 (M^+-H) and 227 ($M^+-C_2H_5$), is in agreement with the cyclised structure 3-methoxy-4-hydroxy-6-ethyl xanthan(17). The formation of 15 and 17 from latifolin(1) and dihydrolatifolin (16) in these dye-sensitized photo-oxidations apparently involves a crucial step of oxidative demethylation followed by cyclisation with the free hydroxyl group of the second ring. A free OH group in ring A para to the methoxy group is essential to start this reaction as latifolin dimethyl ether 2 and dihydrolatifolin dimethyl ether 18 failed to undergo any change when subjected to similar photooxidation.

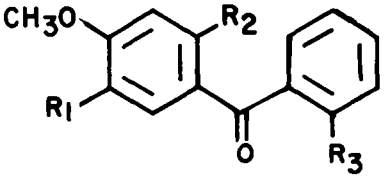


24, $R_1=R_3=H, R_2=OH, R_4=CH_2OH$

25, $R_1=R_2=R_3=OCH_3, R_4=CH_2OH$

26, $R_1=R_3=H, R_2=OH, R_4=CHO$

27, $R_1=R_2=R_3=OCH_3, R_4=CHO$

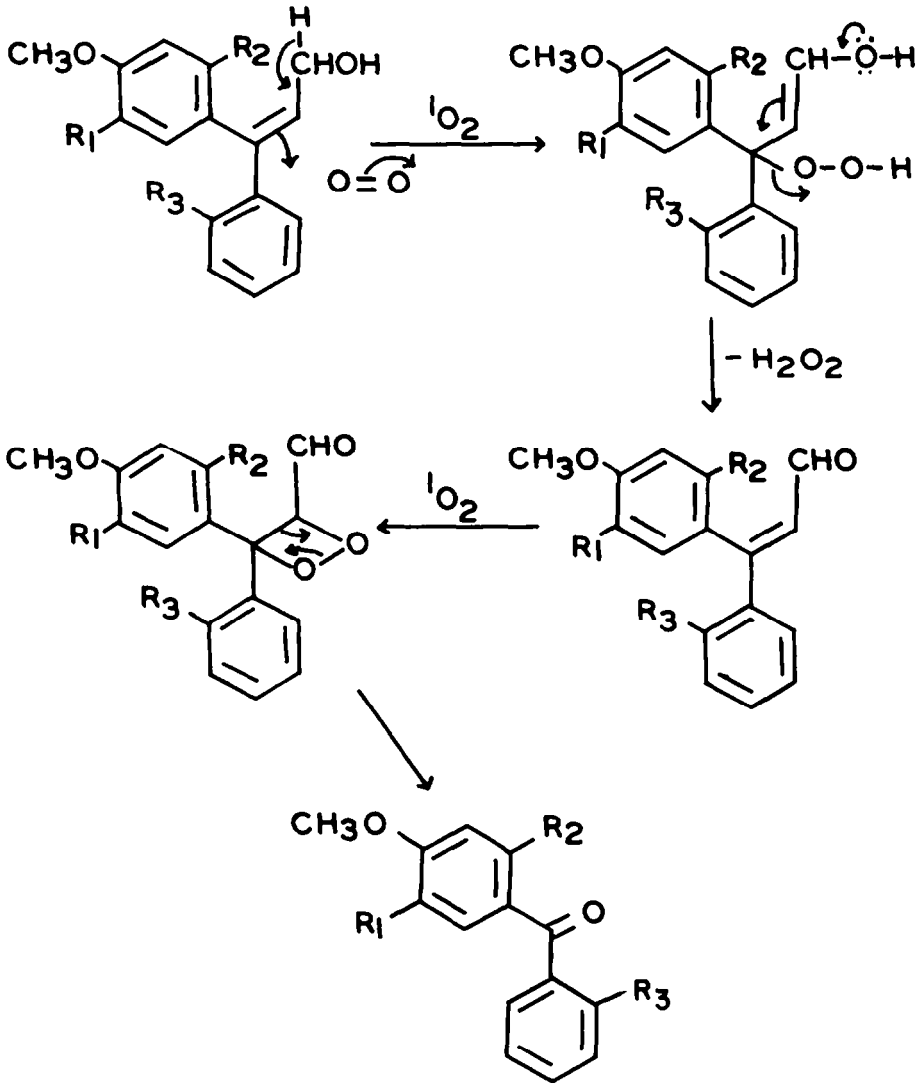


28, $R_1=R_3=H, R_2=OH$

29, $R_1=R_2=R_3=OCH_3$

In order to throw more light on this novel reaction, we studied the photooxidation of the closely related propenyl compound 19 lacking a hydroxyl group in the second ring. Surprisingly it gave a new interesting product which could be assigned the structure 20 as its ^1H NMR spectrum exhibited on methoxyl (δ 3.9), one hydroxyl (δ 5.75, D_2O exchangable) and a methyl group as shown by a new singlet at δ 2.45. Comparison of this spectrum with that of the starting material revealed that the methoxyl peak at δ 3.5 and the doublet due to the side chain methyl group of 19 is absent indicating their involvement

in the formation of the new product 20. Its mass spectrum gave a molecular ion peak at m/z 254 but did not show $M^+-(-CH=CH_2)$ peak as in 15 or $M^+-(CH_2CH_3)$ peak as in 17. Instead this spectrum showed a strong peak at m/z 211 indicating loss of C_2H_3O unit as expected from a 2-methyl benzofuran derivative. On this basis it was assigned the structure as 2-methyl-3-phenyl-5-hydroxy-6-methoxy benzofuran (20). The complete methyl ether, 3-(2,4,5-trimethoxyphenyl)-3-phenyl prop-2-ene (21) again did not undergo any photochemical change under similar conditions.

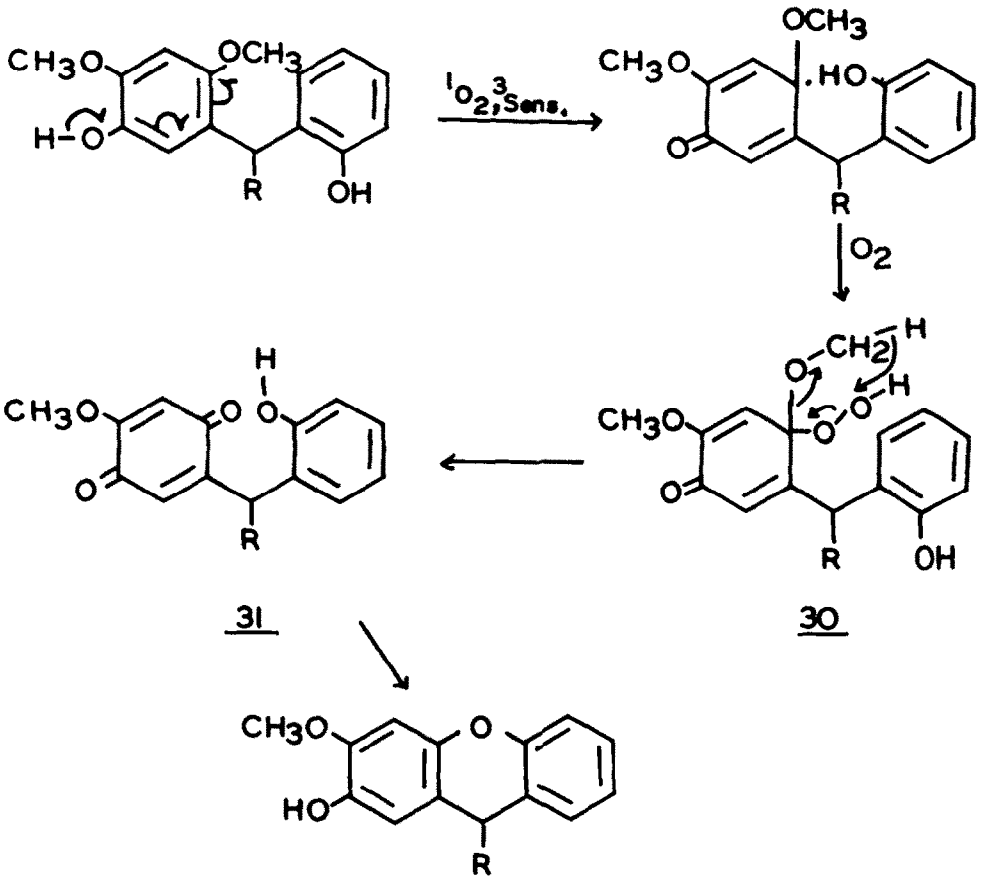


SCHEME I

Apparently the first step in the formation of the benzofuran 20, is again oxidative demethylation. However, the quinonoid intermediate, lacking a hydroxyl group in ring B, involved the propene side chain instead, in this process, finally yielding 20.

Indeed the first step in above photooxidations is oxidative demethylation of the partial methyl ether of the para quinol system in ring A, as 3-(2,4-dimethoxy-5-hydroxyphenyl)-3-phenyl propane (22), prepared by hydrogenation of

propenyl compound 19, gave on similar photooxidation the quinone 23 which could not undergo further cyclisation as it lacked features like ortho hydroxy group in ring B or a propenyl double bond. The structure of 23 was confirmed by its mass spectrum (M^+,256) and ^{1}H NMR spectrum which exhibited the presence of one methoxyl group (δ 3.8) and two shielded aromatic protons (δ 5.95 and 6.6) and the absence of one methoxyl peak at δ 3.7 as well as one D_2O exchangable OH peak at δ 5.25 originally present in ^{1}H NMR spectrum of 22. Scheme II and III depicts the possible mechanism of these oxidative demethylation and cyclisations



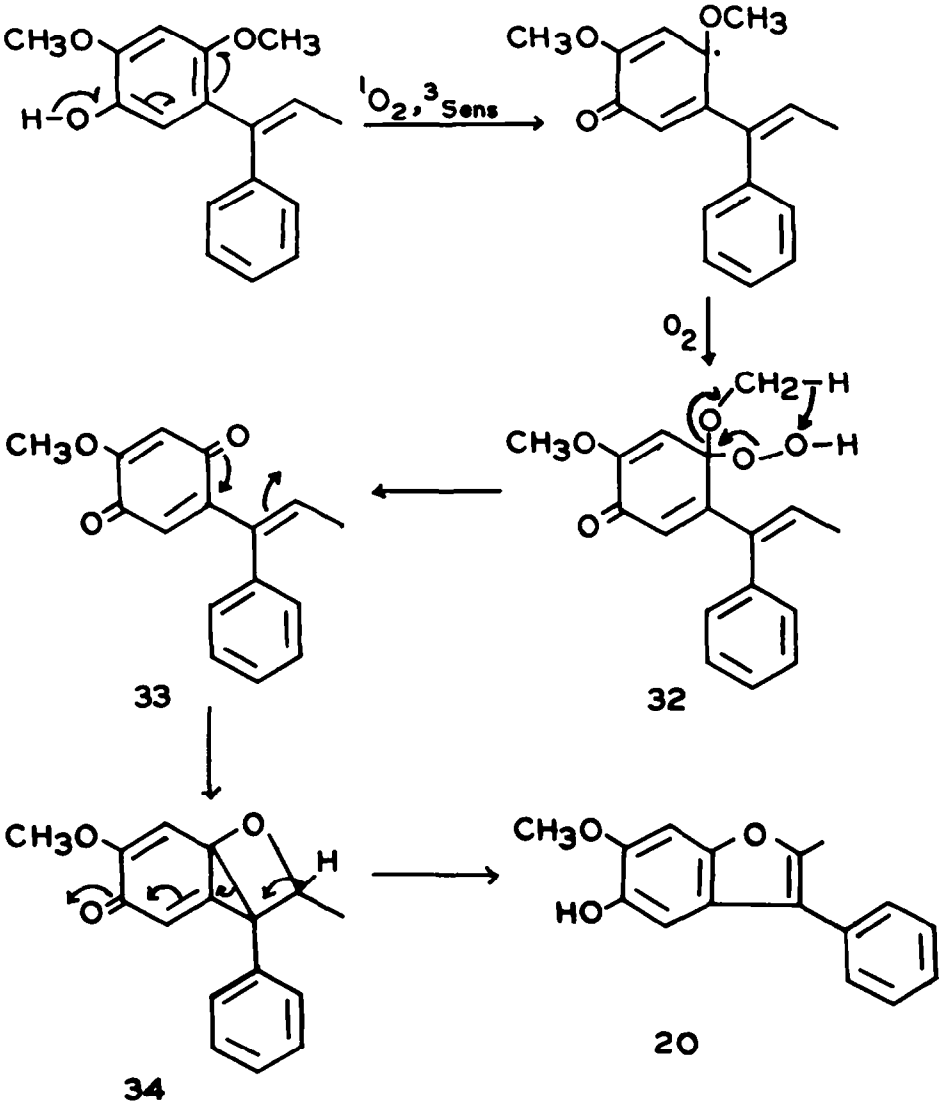
SCHEME II

The primary requirement in these oxidative demethylations is a para quinol partial methyl ether system as present in 1,16,19 and 22. A free phenolic group alone is not sufficient to give the quinone intermediate. The cinnamyl alcohol 24 having one phenolic group was tried next to see whether a side chain allylic hydroxyl group can participate in this cyclisation. It did not give any cyclised product, instead it gave the substituted cinnamaldehyde 26 by oxidation through hydroperoxide intermediate as shown in Scheme I. Similar mechanism involving hydroperoxide intermediates for oxidations of olefins[11] and allyl alcohols[12] have been proposed earlier. The benzophenone 28 is formed by further oxidation of 26. Similarly the fully methylated cinnamyl alcohol 25 also gave the cinnamaldehyde 27 and the benzophenone 29.

The mechanism of dye-sensitized photooxidative demethylation of para quinol partial methyl ethers have been described earlier by Saito et al[13] who postulated the agency of both singlet oxygen and excited triplet sensitizer for the initiating step of hydrogen abstraction from the phenol. The combination of resulting radical with the triplet oxygen followed by elimination of HCHO from the complex finally yields the para quinone. Similar quinonoid intermediates must be forming in the present cases also as evident from the isolation of 23. However, the cyclisation of the quinonoid intermediates to the xanthans 15 and 17 is rather novel and its mechanism is not very clear.

The mechanism for the formation of the benzofuran 20, through the quinone intermediate 33 and 34, is envisaged in Scheme III. Mechanism involving similar intermediates have been postulated earlier[14] for light induced conversion of monosubstituted benzoquinones to benzofurans.

Oxidation of latifolin with free radical initiator like $K_3[(Fe(CN)_6]$ following the procedure of Sarkanen and Willis[15] gave a yellow dimeric product mp.200°(d), (M^+,506) and not the xanthan[15] showing that singlet oxygen and excited triplet sensitizer play a specific role in these dye-sensitized photooxidative cyclisations excluding the possibility of exclusive involvement of free radicals.



SCHEME III

EXPERIMENTAL PROCEDURES

Melting points are uncorrected. IR spectra were recorded on a Perkin Elmer-457 Spectrophotometer. UV spectra were recorded in ethanol solution on a Varian 634 Spectrophotometer. ^{1}H NMR spectra were recorded on a Varian EM-360 (60 MHz) spectrometer. Chemical shifts are reported in ppm δ scale relative to TMS as internal standard. MS spectra were obtained on a Zeol JMS-D300 mass spectrometer.

Irradiation of Latifolin (1)

Latifolin (1, 300 mg) in benzene (300 ml) was irradiated with light from a high pressure mercury lamp filtered through pyrex for 6 hours. The residue obtained after removal of solvent was purified by chromatography over silica gel using benzene as eluant when it gave the cyclopropane 5 (175 mg) which crystallised from ethanol as colourless cubes, m.p.111-12° (Found: C,70.9; H,6.3; $C_{17}H_{18}O_4$ requires C,71.3; H,6.3%). MS: m/z 286 (M^+). ^{1}H NMR ($CDCl_3$): δ 1.00-1.50 (2H,m $-CH_2-$ of cyclopropane ring); 1.71-2.16 (2H,m,benzylic); 4.01 (3H,s,OCH_3), 4.10 (3H,s,OCH_3); 5.3 (1H,s,Ar-OH,D_2O exchangable); 5.8 (1H,s,Ar-OH,D_2O exchangable); 6.66 (1H,s,aromatic); 6.75 (1H,s,aromatic); 6.9-7.3 (4H,m, aromatic); λ_{max}^{nujol} 3580(OH), 3500 (OH) and 1031 cm^{-1} (cyclopropane).

On methylation 5 gave the tetramethoxy compound 6, mp.91°, identical with the product obtained by the photorearrangement of latifolin dimethyl ether (2) (lit[1] mp.92-93°).

Irradiation of 3-(2,4,5-trimethoxyphenyl)-3-phenyl prop-1-ene (3)

3-(2,4,5-trimethoxyphenyl)-3-phenyl propene[4] (3, 300 mg) was photolysed as above when it yielded a mixture (TLC) of two very closely related compounds. These were separated by repeated column chromatography on alumina followed by crystallisation from hexane when it gave 7 (m.p.93-94°) (Found: C,76.1; H,7.1; $C_{18}H_{20}O_3$ requires C,76.1; H,7.0%). MS: m/z 284 (M^+). ^{1}H NMR ($CDCl_3$): δ 1.06-1.41 (2H,m,$-CH_2-$); 1.86-2.50 (2H,m,benzylic); 3.70,3.75 (9H,s,3XOCH_3); 6.35 (1H,s,H_a or H_b); 6.42 (1H,s,H_b or H_a); 7.10 (5H,m,aromatic).

Repeated crystallisation from hexane of the residue from mother liquor gave 8 (50 mg), m.p.69-71° (Found: C,76.4; H,7.3; $C_{18}H_{20}O_3$ requires C,76.1; H,7.0). MS: m/z 284 (M^+). ^{1}H NMR ($CDCl_3$): δ 1.05-1.42 (2H,m,$-CH_2-$); 1.85-2.50 (2Hm,benzylic); 3.45, 3.53 and 3.56 (9H,3s,3XOCH_3); 6.18 (1H,s,H_a or H_b); 6.20 (1H,s,H_b or H_a); 6.91 (5H,m,aromatic).

Irradiation of 3-(2,4-dimethoxyphenyl)-3-phenyl propene (4)

3-(2,4-dimethoxyphenyl)-3-phenyl propene[4] (4,500 mg) was photolysed as described earlier when it gave a mixture. On $AgNO_3$ impregnated TLC plates it gave two spots corresponding to cis 10 and trans 9 isomers which could not be separated. The mixture gave the following spectral data. MS: m/z 254 (M^+); λ_{max}^{KBr} 1032 cm^{-1} (cyclopropane). ^{1}H NMR (CCl_4): δ 1.25 (2H,m,$-CH_2-$); 1.90 (2H,m, benzylic); 3.60, 3.68 (6H,s,2XOCH_3 for cis isomer); 3.76 and 3.81 (6H,s, 2XOCH_3 for trans isomer); 6.40 (2H,m,H_a and H_c); 6.80-7.25 (6H,m,H_b and aromatic).

Synthesis of 1-(2,4,5-trimethoxyphenyl)-1-(2-methoxyphenyl cyclopropane (13)

To a stirred suspension of Zn-Cu couple (3.9 g) and catalytic amount of cuprous iodide in dry ether (400 ml), was added methylene iodide (4 g) and 1-(2,4,5-trimethoxyphenyl)-1-(2-methoxyphenyl) ethylene[7] (11, 4.5 g). The reaction mixture was gently refluxed for 24 hr. and then cooled and filtered. The filtrate was washed with $NaHCO_3$, brine and dried. The solvent was removed and the residue purified by column chromatography over silica gel using hexane as the eluant when it gave 14 which crystallised from hexane as colourless

plates, m.p.120-22°. (Found: C,72.1; H,6.6. $C_{19}H_{22}O_4$ requires C,72.6; H,7.0%). $\lambda_{max}^{CHCl_3}$ 1034 cm^{-1} (cycloprepane). MS: m/z 314 (M^+), ^1H NMR ($CDCl_3$): δ 1.12 (4H,s,2x-CH_2-); 3.75, 3.81 and 3.90 (12H,s,4xOCH_3); 6.43 (1H,s,aromatic); 6.7-7.3 (5H,m,aromatic).

Photooxidation of Latifolin (1)

Latifolin (1, 200 mg) in CCl_4 (200 ml) containing a suspension of rose bengal (100 mg) adsorbed on silica gel (2 g) was irradiated with light from tungsten lamps (600 W) while a gentle stream of air was bubbled through the solution to keep the suspension stirred. After 24 hrs. (TLC), the solution was filtered and solvent removed under reduced pressure. The residue was chromatographed over silica gel using hexane and benzene as eluants. Hexane-benzene (1:1) eluate (250 ml) on evaporation afforded 15 which crystallised from methanol as light needles (100 mg), mp. 80-81° (Found: C,75.7; H,5.3. $C_{16}H_{14}O_3$ requires C,75.9; H,5.5%). MS: m/z 254 (M^+), 253 (M^+-H), 227 (M^+-C_2H_3). ^1H NMR ($CDCl_3$): δ 3.8 (3H,s,OCH_3); 4.45 (1H,s,J=8Hz, -$\underset{|}{C}$-CH=CH_2); 4.9 (1H,m,-CH=C$\underline{H}_2$); 5.2 (1H,m,-CH=C$\underline{H}_2$); 5.25 (1H,s,-O$\underline{H}$,D_2O exchangable); 5.9 (1H,m,-$\underset{|}{C}$H-C$\underline{H}$=CH_2); 6.5 (1H,s,aromatic), 6.65 (1H,s,aromatic); 7.1 (4H,m,aromatic).

Photooxidation of dihydrolatifolin (16)

Dihydrolatifolin (16, 200 mg) in CCl_4 (200 ml) was photooxidised as above. After 24 hrs, the reaction mixture was worked up as usual and the residue chromatographed over silica gel using hexane and benzene as eluants. Hexane-benzene (1:1, 250 ml) eluate yielded 17 as viscous liquid (120 mg) which was further purified by preparative TLC followed by distillation under vacuum (0.1 mm Hg) at 190° (bath) when it was obtained as a colourless liquid (Found: C,74.7; H,5.9. $C_{16}H_{16}O_3$ requires C,75.0; H,6.3%). MS: m/z 256 (M^+), 255 (M^+-H), 227 (M^+-C_2H_5). ^1H NMR ($CDCl_3$): δ 0.7 (3H,t,-CH_2C$\underline{H}_3$); 1.7 (2H,m,-C$\underline{H}_2$$CH_3$); 3.8 (3H,s,$OCH_3$); 3.82 (1H,t,-C$\underline{H}$$CH_2CH_3$); 5.2 (1H,s,-O$\underline{H}$,$D_2O$ exchangable); 6.6 (1H,s, aromatic); 6.7 (1H,s,aromatic); 7.0 (4H,m,aromatic).

Photooxidation of 3-(2,4-dimethoxy-5-hydroxyphenyl)-3-phenyl prop-2-ene (19)

3-(2,4-dimethoxy-5-hydroxyphenyl)-3-phenylprop-2-ene[10] (19,200 mg) in CCl_4 (200 ml) was photooxidised as above. After 48 hrs. the reaction was worked up as usual and the residue chromatographed over silica gel when it gave 20 which crystallised from methanol as colourless plates (125 mg), m.p.121°C (Found: C,75.1; H,5.2. $C_{16}H_{14}O_3$ requires C,75.6; H,5.5%). MS: m/z 254 (M^+), 239 (M^+-CH_3), 211 (M^+-C_2H_3O). ^1H NMR ($CDCl_3$): δ 2.45 (3H,s,-$\underset{|}{C}$-C$\underline{H}_3$); 3.9 (3H,s, OCH_3); 5.75 (1H,s,O$\underline{H}$,D_2O exchangable); 6.9 & 7.0 (2H,2s,para aromatic protons); 7.4 (5H,m,aromatic).

Hydrogenation of 3-(2,4-dimethoxy-5-hydroxyphenyl)-3-phenyl prop-2-ene (19)

A solution of 3-(2,4-dimethoxy-5-hydroxyphenyl)-3-phenyl prop-2-ene[10] (19, 1 g) in ethyl alcohol (200 ml) containing Pd/C (10%, 100 mg) was stirred in H_2 gas until one mole of the gas was absorbed. The reaction mixture was then filtered and the solvent removed to furnish 22 which crystallised from methanol as colourless needles (800 mg), mp. 58°. (Found: C,74.6; H,7.2. $C_{17}H_{20}O_3$ requires C,75.0; H,7.4%). MS: m/z 272 (M^+). ^1H NMR ($CDCl_3$):δ0.82 (3H,t,-CH_2C$\underline{H}_3$); 1.93 (2H,m,-$\underset{|}{C}$HC$\underline{H}_2$$CH_3$); 3.7 (3H,s,$OCH_3$); 3.8 (3H,s,$OCH_3$); 4.2 (1H,t,-$\underset{|}{C}$H-$CH_2CH_3$); 5.25 (1H,s,O$\underline{H}$,$D_2O$ exchangable); 6.5 & 6.9 (2H,2s,para aromatic protons); 7.5 (5H,m,aromatic).

Photooxidation of 22

3-(2,4-dimethoxy-5-hydroxyphenyl)-3-phenyl propane (22, 200 mg)in CCl_4 (200 ml) was photooxidised as earlier for 48 hrs. when the reaction appeared to be complete. Removal of solvent from the filtrate and chromatography of

the residue over silica gel yielded 23 which crystallised from methanol as yellow needles (140 mg), mp. 152° (Found: C,74.7; H,6.6. $C_{16}H_{16}O_3$ requires C,75.0; H,6.3%). MS: m/z 256 (M^+-CH_3), 228 (M^+-CO), 227 ($M^+-CH_2CH_3$). ^1H NMR ($CDCl_3$): δ 0.9 (3H,t,$-CH_2CH_3$); 1.9 (2H,m,$-\underline{CH}CH_2CH_3$); 3.8 (3H,s,OCH_3); 4.1 (1H,t,$-\underline{CH}CH_2CH_3$); 5.95 & 6.6 (2H,2s,para aromatic protons; 7.3 (5H,m,aromatic).

Photoexidation of 3-(2-hydroxy-4-methoxyphenyl)-3-phenyl allyl alcohol (24)

3-(2-hydroxy-4-methoxyphenyl)-3-phenyl allyl alcohol[4] (24, 550 mg) in CCl_4 (500 ml) was photoexidised as earlier for 48 hrs. The reaction mixture was worked up and the residue chromatographed over silica gel eluting the column with benzene when it gave the benzephenone 28 which crystallised from methanol as colourless needles, (Found: C,74.1; H,5.9. $C_{14}H_{12}O_3$ requires C,73.7; H,5.3%). MS: m/z 228 (M^+). ^1H NMR ($CDCl_3$): δ 3.8 (3H,s,OCH_3); 6.5 (1H,s,OH,D_2O exchangable), 7.4-7.6 (8H,m,aromatic protons).

Further elution with benzene (200 ml) gave 26 as viscous liquid MS: m/z 254 (M^+). ^1H NMR ($CDCl_3$): δ 3.8 (3H,s,OCH_3), 6.6 (1H,d,$-\underline{C}=C\underline{H}CHO$); 7.5-7.7 (8H,m,aromatic); 9.7 (1H,d,$-\underline{C}=CH\underline{C}HO$).

Photoexidation of 3-(2,4,5-trimethoxyphenyl)-3-(2-methoxy phenyl) allyl alcohol (25)

3-(2,4,5-trimethoxyphenyl)-3-(2-methoxyphenyl) allyl alcohol[4] (25, 500 mg) in CCl_4 (500 ml) was photoexidised as earlier for 48 hrs. Chromatography of the mixture over silica gel using benzene as eluant gave 27 as pale yellow powder (TLC pure) from methanol. mp.107-8° (Found: C,69.2; H,5.9. $C_{19}H_{20}O_5$ requires C,69.5; H,6.1%). MS: m/z 328 (M^+). ^1H NMR ($CDCl_3$); δ 3.20 (3H,s,OCH_3), 3.8 (12H,m,4xOCH_3) 6.5 (1H,d,$-\underline{C}=C\underline{H}CHO$), 6.7 (1H,s,aromatic); 6.8 (1H,s,aromatic); 7.0 (4H,m,aromatic); 9.45 (1H,d,$-\underline{C}=CH\underline{C}HO$).

Further elution with benzene yielded 29 which crystallised as light yellow prisms from methanol, mp.92-3° (Found: C,67.1; H,6.4.$C_{17}H_{18}O_5$ requires C,67.5; H,6.0%). MS: m/z 302 (M^+). ^1H NMR ($CDCl_3$): δ 3.8 (12H,m,4xOCH_3); 6.65 (1H,s,aromatic); 6.75 (1H,s,aromatic); 7.05 (4H,m,aromatic).

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