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THE STRUCTURE OF FLAVANONOL-RED[1]

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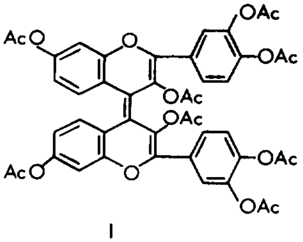
A series of red pigments was obtained from flavanonols in amorphous state when the latter were boiled with acetic anhydride and sodium acetate.[2,3] H. Pacheco proposed the bisflavone type structures for these amorphous pigments: e.g., structure I for the pigment obtained from taxifolin.[3,4] A few years ago, red pigments were obtained in crystalline state in the cases of flavanonol itself (m.p. 208-210°C), 4'-bromo-3-hydroxyflavanone (m.p. 299-300°C), and ampeloptin (m.p. 223-224°C). The structural study reported herein was made on the pigment (tentatively named flavanonol-red[1]) obtained from 3-hydroxyflavanone.

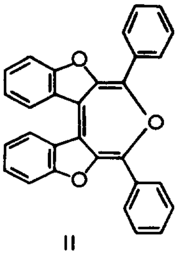
Flavanonol-red (II), $C_{30}H_{18}O_3$, showed absence of hydroxyl, acetoxyl and carbonyl absorptions but exhibited ν_{max}^{Nujol} 750 and 680 cm^{-1} in the I.R. spectrum. The visible spectrum showed λ_{max}^{THF} 457, 487 and 525 mμ (log ε 4.18, 4.58 and 4.74), characteristic of flavanonol pigments. On catalytic hydrogenation with platinum oxide in dioxane flavanonol-red resulted in absorption of three moles of hydrogen to give a hexahydro compound (III), $C_{30}H_{24}O_3$, m.p. 183-184°C, which also showed no absorption in hydroxyl, acetoxyl and carbonyl regions of the I.R. spectrum. Ozonization of II followed by reductive decomposition afforded benzyl alcohol and salicylic acid. Hydrogenolysis of II with metallic sodium in liquid ammonia by Tomita's method[5] afforded a dihydroxy compound (IV), $C_{30}H_{26}O_3$, m.p. 154-155°C,

ν_{max}^{Nujol} 3440 cm^{-1}, λ_{max}^{EtOH} 282 mμ (log ε 3.85). IV formed a diacetate (V), $C_{34}H_{30}O_5$, m.p. 110-112°C. When II was heated for one hour in glacial acetic acid containing a few drops of sulfuric acid, a diketo-diphenol (VI), $C_{30}H_{22}O_5$, m.p. 211-212°C (dec.), ν_{max}^{Nujol} 3300, 1640, 880 cm^{-1}, λ_{max}^{EtOH} 263 and 300 mμ (log ε 4.40 and 4.31), was formed in good yield. VI, which gave a positive test with a mixture of ferricyanide and ferric salts, was derived to a diketo-diacetate (VII), $C_{34}H_{26}O_7$, m.p. 162.5-163°C, and a diketo-dimethyl ether (VIII), $C_{32}H_{26}O_5$, m.p. 194-195°C. The I.R. spectrum of VIII exhibited strong absorptions at 1660, 880 and 700 cm^{-1} and the U.V. spectrum had λ_{max}^{EtOH} 262 and 300 mμ (log ε 4.37 and 4.34). Boiling this diketo-diphenol (VI) with acetic anhydride and sodium acetate did not regenerate the red pigment (II), but only formed VII. Catalytic reduction of the diketo-diacetate (VII) over palladium-on-carbon gave a tetrahydro-diketo-diacetate, $C_{34}H_{30}O_5$, m.p. 112°C, which was identical with the diacetate (V) described above. Similarly, catalytic reduction of the diketo-dimethyl ether (VIII) gave a tetrahydro derivative (IX), $C_{32}H_{30}O_3$, m.p. 99-100°C, the I.R. spectrum of which had no absorption in the hydroxyl and carbonyl regions. Reduction of the diketo-dimethyl ether (VIII) with sodium borohydride in boiling dioxane-methanol resulted in the formation of a dihydroxy-dimethyl ether (X), $C_{32}H_{30}O_5$, m.p. 178-179°C (dec.), which was also obtained on the reduction of VIII with lithium aluminum hydride in the cold. The I.R. spectrum of X exhibited the absorption at 3300 cm^{-1}, but no absorption at 1660 or 880 cm^{-1}.

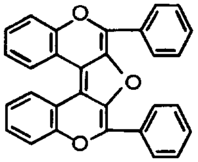
Ozonolysis of the diketo-dimethyl ether (VIII) afforded benzoic acid and a yellow crystal (XI), $C_{18}H_{14}O_5$, m.p. 159-160°C, ν_{max}^{Nujol} 1750, 1820, 770 cm^{-1}, 700 cm^{-1}-band of VIII disappeared, λ_{max}^{EtOH} 300 mμ (log ε 3.98). From these data, XI was assumed to be bis(o-methoxyphenyl)maleic anhydride, which was confirmed through its synthesis from salicylaldehyde methyl ether.



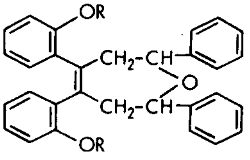
I



II

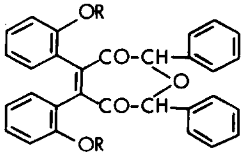


II'



IV R=H

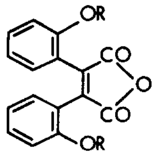
V R=COCH$_3$



VI R=H

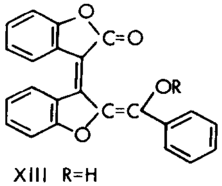
VII R=COCH$_3$

VIII R=CH$_3$



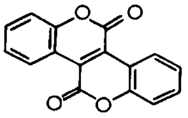
XI R=CH$_3$

XVI R=H



XIII R=H

XIV R=CH$_3$



XV

Based on the foregoing experimental facts, the structure II was presented for flavanonol-red and then the respective compounds obtained by the reduction described above may be shown by the following formulas (III-VIII). But, the possibility of formula II' cannot be neglected exclusively from the above-mentioned results.

When flavanonol-red (II) was irradiated with sun light or ultraviolet light in ethyl acetate in the presence of the air at the ordinary temperature, the red color disappeared after a few minutes and it gave a green colored crystal, which was named photoflavanonol-red (XII), $C_{30}H_{18}O_5$, m.p. 218-220°C, ν_{max}^{Nujol} 1750, 1740, 1660, 1620, 1600, 1500, 770, 765 cm^{-1}; λ_{max}^{EtOH} 234, 315 and 391 mμ (log ε 4.65, 4.23 and 4.45), NMR no peak except in aromatic area (m). Hydrolysis of XII with alkali afforded one mole of benzoic acid and one mole of a hydroxy compound (XIII), $C_{23}H_{14}O_4$, m.p. 275–280°C, ν_{max}^{Nujol} 3270, 1700, 1650 cm^{-1}, λ_{max}^{EtOH} 312 and 391 mμ (log ε 4.03 and 4.30), which was reverted to XII by benzoylation. With dimethyl sulfate and potassium carbonate in dry acetone XIII gave a monomethyl ether (XIV), $C_{24}H_{16}O_4$, m.p. 182–183°C, ν_{max}^{Nujol} 1740, 1650, 1620, 1590, 1460, 755, 700 cm^{-1}; λ_{max}^{EtOH} 237, 243, 312 and 389 mμ (log ε 4.50, shoulder, 4.29 and 4.45), NMR δ 3.90 (s, 3H) and 7.00–8.55 ppm (m, 13H). When the hydroxy compound (XIII) was oxidized with potassium permanganate in dry acetone or with the air in a mixture of aqueous sodium hydroxide, tetrahydrofuran and ethanol under refluxing, it afforded benzoic acid and a dilactone (XV), $C_{16}H_8O_4$, m.p. 295–296°C; ν_{max}^{Nujol} 1725, 1605, 1590, 1310, 1245, 1165, 1110, 775, 755, 735 cm^{-1}; λ_{max}^{EtOH} 253, 268 and 380 mμ (log ε 3.98, 3.92 and 4.10), which was identified with the authentic sample.[6]

On ozonization, XIV afforded methyl benzoate and a dihydroxy-anhydride (XVI), $C_{16}H_{10}O_5$, m.p. 160–161°C, ν_{max}^{Nujol} 3480, 1830, 1750, 1645, 1600, 950, 930, 780, 760 cm^{-1}, which was derived to bis(o-methoxyphenyl)maleic anhydride (XI) by methylation with dimethyl sulfate and alkali. The formation of methyl benzoate in the above ozonolysis of XIV excluded the formula II' for flavanonol-red distinctly. All the reactions described above supported the formula II.

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