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THE SYNTHESIS OF QUINOCHALCONES

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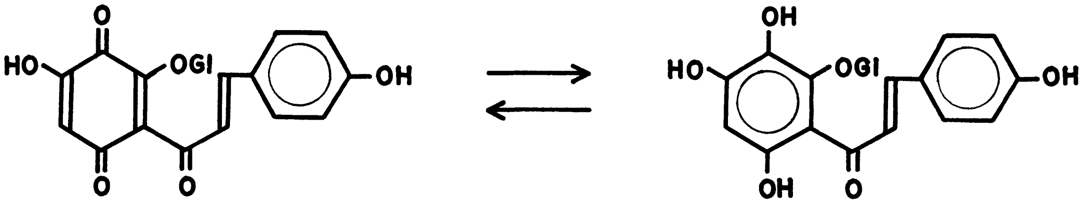
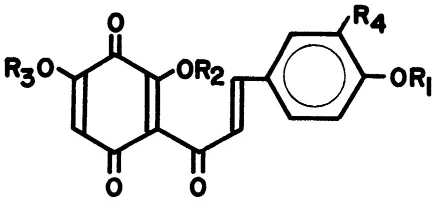
2',4,4'-Trihydroxy-, 2',4-dihydroxy-4'-methoxy-, and 2'-hydroxy-4,4'-dimethoxy-3',6'-quinochalcone (VI, X, and XIII) were obtained by the oxidation of the corresponding chalcones with nitric acid, and their properties have been compared with those of the red pigment from the flowers of *Carthamus tinctorius* L.

In 1960, Seshadri[1] proposed quinochalcone structure I, named carthamon, for the red coloring component of the flowers of *Carthamus tinctorius* L, which conventionally being called carthamin,[2] and he reported that this pigment (I) can be reduced to the yellow chalcone (II) by sulfur dioxide and reoxidized to the original material by peroxidase. However, the synthetic studies of I have not been reported, and hitherto no detailed investigation has been known on the synthesis of such quinochalcones. In connection with the synthetic studies of carthamin, we have reported the synthesis of 2',3',4,4',6'-pentahydroxychalcone (III)[3] corresponding to the aglycon (II) and 2'-methoxy-3',4,4',6'-tetrahydroxychalcone[4] which is an analog of II, however, no quinochalcones could be obtained by the peroxidase oxidation of these two chalcones. In the present paper, we will describe the synthesis of new quinochalcones, 2',4,4'-trihydroxy-3',6'-quinochalcone (VI) corresponding to the aglycon of I and its mono- and di-methyl ether (X and XIII) and comparison of their properties with those of the natural red pigment.



(I) (II)



(V) $R_2=R_4=H$, $R_1=R_3=CH_2OCH_3$

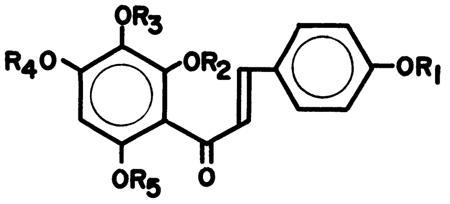
(VI) $R_1=R_2=R_3=R_4=H$

(IX) $R_1=CH_2OCH_3$, $R_2=R_4=H$, $R_3=CH_3$

(X) $R_1=R_2=R_4=H$, $R_3=CH_3$

(XI) $R_1=CH_3$, $R_2=R_3=H$, $R_4=NO_2$

(XIII) $R_1=R_3=CH_3$, $R_2=R_4=H$



(III) $R_1=R_2=R_3=R_4=R_5=H$

(IV) $R_1=R_2=R_3=R_4=R_5=CH_2OCH_3$

(VII) $R_1=CH_2OCH_3$, $R_2=R_3=R_4=R_5=CH_3$

(VIII) $R_1=H$, $R_2=R_3=R_4=R_5=CH_3$

(XII) $R_1=R_2=R_3=R_4=R_5=CH_3$

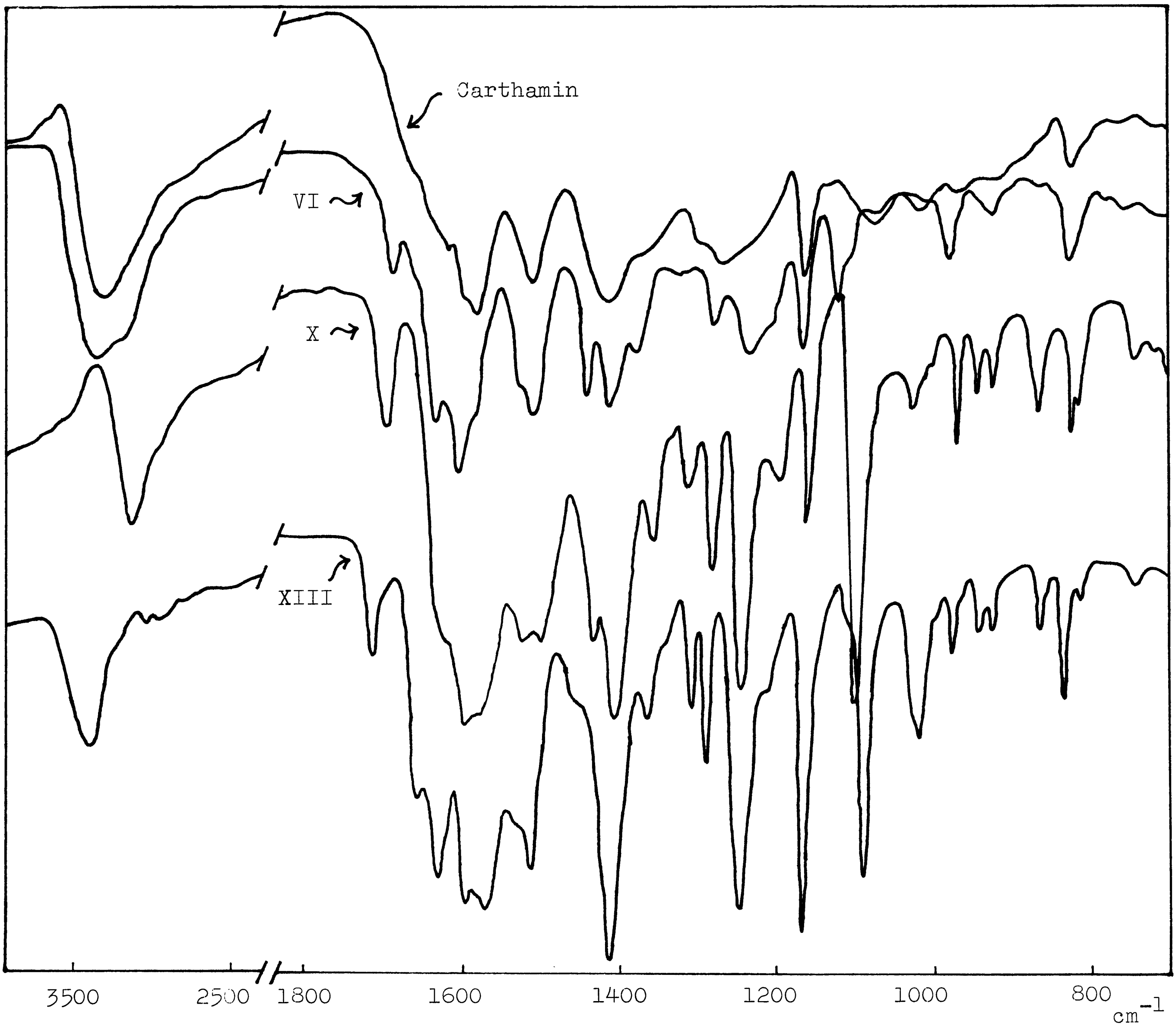


Fig. 1. Infrared spectra of 2',4,4'-trihydroxy-, 2',4-dihydroxy-4'-methoxy- and 2'-hydroxy-4,4'-dimethoxy-3',6'-quinochalcone (VI, X and XIII) and carthamin. (KBr disk).

2',4,4'-Trihydroxy-3',6'-quinochalcone (VI), reddish plates from acetic acid, mp 234-236°C: λ_{max} (ethanol), 412(log ε, 4.41), 310(3.97) and 260 nm (3.90), was obtained by the oxidation of III with nitric acid in ethanol, or by the demethoxymethylation of 2'-hydroxy-4,4'-bis(methoxymethoxy)-3',6'-quinochalcone (V), mp 142-143°C, which was prepared by the nitric acid oxidation of 2',3',4,4',6'-pentakis-(methoxymethoxy)chalcone (IV) in acetic acid containing 6 N hydrochloric acid.

Since this chalcone was unstable in solution and an attempted methylation by the usual way was not achieved, its methyl ethers were prepared by the following methods, respectively. 2',4-Dihydroxy-4'-methoxy-3',6'-quinochalcone (X), mp 252-254°C, λ_{max} (chloroform), 264, 300 and 414 nm, was obtained by the demethoxymethylation of 2'-hydroxy-4'-methoxy-4-methoxymethoxy-3',6'-quinochalcone (IX), mp 155-156°C, which was prepared by the nitric acid oxidation of 2',3',4',6'-tetramethoxy-4-methoxymethoxychalcone (VII) obtained by the condensation of 2,3,4,6-tetramethoxyacetophenone with p-methoxymethoxybenzaldehyde. Similarly, 2'-hydroxy-4,4'-dimethoxy-3',6'-quinochalcone (XIII), mp 188-189°C, λ_{max} (chloroform), 261(log ε, 4.10), 297(4.06) and 412 nm (4.54), was obtained by the oxidation of 2',3',4,4',6'-pentamethoxychalcone (XII)$^{3)}$ with nitric acid in acetic acid. The direct oxidation of 2',3',4',6'-tetramethoxy-4-hydroxychalcone (VIII), mp 120-121°C, prepared by the demethoxymethylation of VII gave 2',4-dihydroxy-3-nitro-4'-methoxy-3',6'-quinochalcone (XI), mp 202-204°C, λ_{max} (chloroform), 277 (log ε, 4.32) and 382 nm (4.54). The structures of these quinochalcones were determined by the studies of their uv, ir and nmr spectra and by elemental analyses.

The infrared spectra of these quinochalcones (VI, X and XIII) and the red pigment (carthamin) are shown in Fig. 1. Although the synthetic quinochalcones showed a carbonyl absorption band about at 1700 cm^{-1} which is caused by their quinonoid structure, no such absorption band could be observed in the case of carthamin. Further, as described in the previous paper,$^{4)}$ carthamin showed a characterestic absorption band at 520 nm in its electronic spectrum, but, these synthetic quinochalcones have not exhibited absorption maxima in such long wavelength region. From these results, it is thought that the structure of Seshadri's carthamon (I) for the red pigment is not always reasonable and the structure of carthamin is a more long conjugated system.

Reference

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