CHEMISTRY LETTERS, pp. 335-338, 1974. Published by the Chemical Society of Japan

THE SYNTHESES AND PROPERTIES OF TWO ANALOGS OF CARTHAMIN

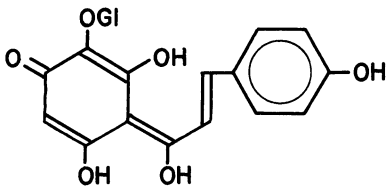
Heitaro OBARA, Jun-ichi ONODERA, and Satoshi ABE
Department of Applied Chemistry, Faculty of
Engineering, Yamagata University, Yonezawa 992

Two analogs of carthamin, 3'-methoxy-2',4,4',6'-tetrahydroxychalcone (VII) and 2'-methoxy-3',4,4',6'-tetrahydroxychalcone (XI) have been prepared and their properties compared with those of carthamin. The disagreement of the behavior between these synthetic chalcones and carthamin has not supported the conventional structure of carthamin.

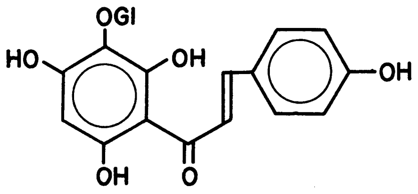
In 1930, Kuroda[1)] proposed structure I for carthamin, the red coloring matter of the flowers of Carthamus tinctorius, and she described besides the red carthamin a yellow unstable tautomeric form, isocarthamin (II), which is very liable to convert into the stable carthamin. On the other band, Seshadri[2)] proposed that the yellow hydroxychalcone (III) which is the main component of the flowers should be called carthamin, and the red dye which is called conventionaly carthamin by Kuroda given the constitution of the quinochalcone, carthamon (IV), and he reported that IV was obtained by oxidation of III in the presence of peroxidase.

In connection with the synthetic studies of carthamin, we have reported the synthesis of 2',3',4,4',6'-pentahydroxychalcone[3)] corresponding to the aglycon of II or III and its isomerization into 4',5,6,7- and 4',5,7,8-tetrahydroxyflavanone (isocarthamidin and carthamidin)[4)]. In the present paper, the syntheses of two analogs of II and III, 3'-methoxy-2',4,4',6'-tetrahydroxychalcone (VII) and 2'-methoxy-3',4,4',6'-tetrahydroxychalcone (XI), and comparison of their properties with those of carthamin will be described.

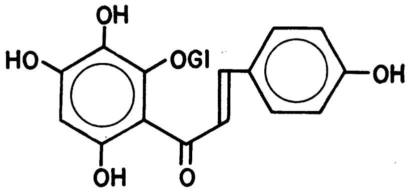
The condensation of 3-methoxy-2,4,6-tris(methoxymethoxy)acetophenone (V) with p-methoxymethoxybenzaldehyde afforded 3'-methoxy-2',4,4',6'-tetrakis(methoxymethoxy)chalcone (VI) as a pale yellow viscous oil, which was hydrolyzed with



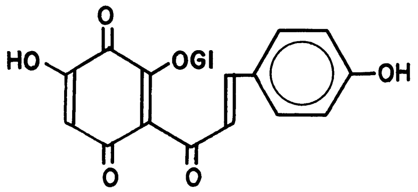
(I)



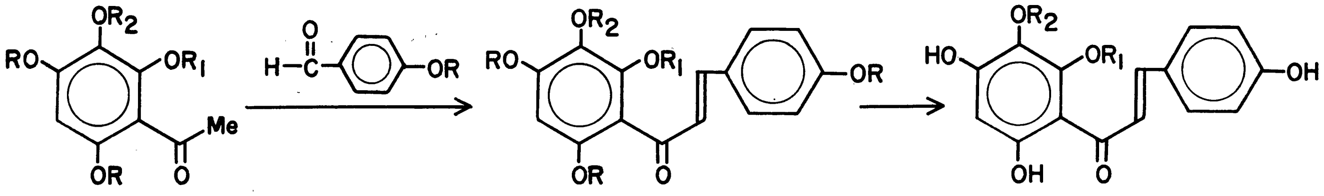
(II)



(III)



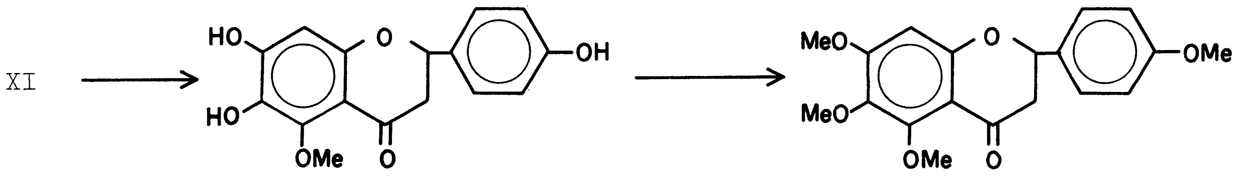
(IV)



(V) R_1=R, R_2=Me (VI) R_1=R, R_2=Me (VII) R_1=H, R_2=Me

(VIII) R_1=H, R_2=R (X) R_1=Me, R_2=R (XI) R_1=Me, R_2=H

(R=$MeOCH_2$-)



(XII) (XIII)

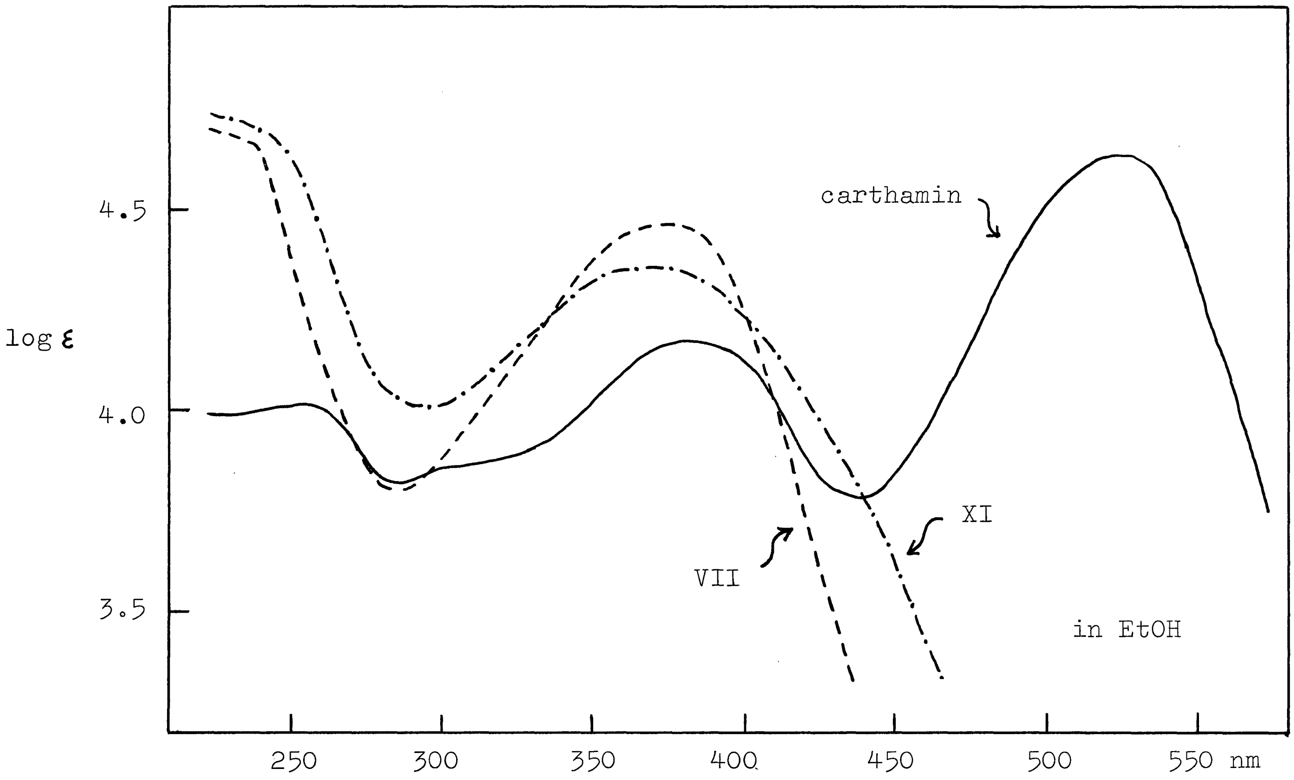


Fig. 1. Electronic spectra of carthamin, VII, and XI.

dilute hydrochloric acid in methanol to give VII as yellow crystals, mp 169-171°C.

Similarly, 2'-methoxy-3',4,4',6'-tetrahydroxychalcone (XI), orange yellow crystals, mp 190-191°C, was obtained by the hydrolysis of 2'-methoxy-3',4,4',6'-tetrakis(methoxymethoxy)chalcone (X) prepared by methylation of the condensation product (IX) of 2-hydroxy-3,4,6-tris(methoxymethoxy)acetophenone (VIII) with *p*-methoxymethoxybenzaldehyde. The structures of these chalcones were identified by elemental analyses, by the studies of their UV, IR, and NMR spectra.

The structure of XI was further confirmed by its conversion into 5-methoxy-4',6,7-trihydroxyflavanone (XII), mp 232-234°C, by acid. The trimethyl ether (XIII) of XII was completely identical with an authentic sample of 4',5,6,7-tetramethoxyflavanone[5].

The electronic spectra of these synthetic analogs (VII and XI) and carthamin are shown in Fig. 1. Since the tautomerism exhibits between carthamin (I) and isocarthamin (II) as described at the biggining, the absorption spectrum of VII must be similar to that of carthamin, but, these two spectra were not resemble at all. Actually, the chalcone (VII) is stable compound and has not showed an unstable behavior such as carthamin.

Further, an attempted oxidation of XI in the presence of peroxidase for an expectation of an analog of carthamon (IV) was not achieved.

From these results, the constitution assigned by Kuroda or Seshadri to carthamin should be subjected to reexamination.

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(Received January 28, 1974)