

CIII.—*The Constitution of Carthamin. Part II.*  
*β-Carthamidin Pentamethyl Ether and its Synthesis.*

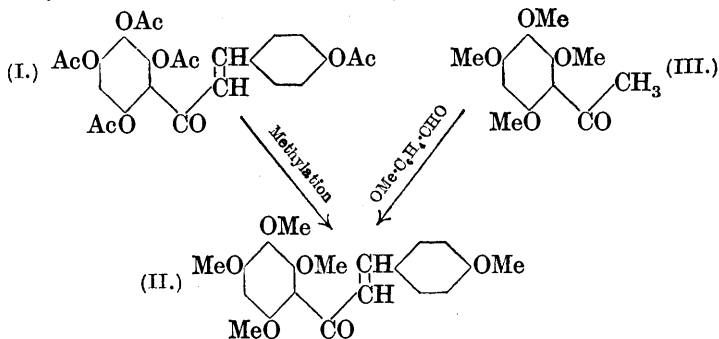
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ONE of the chief hindrances to the study of carthamin and carthamidin, namely, their resistance to methylation, has now been removed.  $\beta$ -Acetylcarthamidin (I) has been methylated by Freudenberg's method (*Annalen*, 1923, **433**, 236) : the product,  $\beta$ -*carthamidin pentamethyl ether* (II), is identical with synthetic 2 : 3 : 4 : 6-tetramethoxyphenyl 4-methoxystyryl ketone.

Carthamin, therefore, which has long been considered a specially complex colouring matter, is a member of a typical class, the hydroxychalkones : it may, however, assume the quinonoid (see formula VII of the preceding paper) or quinhydrone form.

2 : 3 : 4 : 6-Tetramethoxyacetophenone (III) is produced in almost theoretical yield from 1 : 2 : 3 : 5-tetramethoxybenzene and acetyl chloride in the presence of aluminium chloride but in the absence of a solvent (compare Bargellini and Bini, *Atti R. Accad.*

*Lincei*, 1910, **19**, 595; Bargellini, *Gazzetta*, 1914, **49**, 47; Chapman, Perkin, and Robinson, *J.*, 1927, 3020).



#### EXPERIMENTAL.

*Methylation of  $\beta$ -Acetylcarthamidin.*—50% Potassium hydroxide solution (7 c.c.) was added with great caution to a solution of methyl sulphate (3 c.c.) and  $\beta$ -acetylcarthamidin (0.2 g.) in methyl alcohol (15 c.c.) in an atmosphere of hydrogen: to complete the reaction, a little heat was supplied. When water was added to the product,  $\beta$ -carthamidin pentamethyl ether (II) separated as a fine precipitate (0.05—0.06 g.). A chloroform solution of the products of several preparations was evaporated and the methyl ether, obtained in prisms, was washed with ether and recrystallised from methyl alcohol; m. p. 112° (Found: C, 66.8; H, 6.0.  $C_{20}H_{22}O_6$  requires C, 67.0; H, 6.1%).

$\beta$ -Carthamidin pentamethyl ether is almost colourless (very pale yellow) and is readily soluble in chloroform and benzene and fairly readily soluble in ether and alcohol; it gives a red solution in concentrated sulphuric acid, and is coloured red by concentrated hydrochloric acid, showing distinct halochromy.

*Synthesis of  $\beta$ -Carthamidin Pentamethyl Ether (2:3:4:6-Tetramethoxyphenyl 4-Methoxystyryl Ketone).*—Pyrogallol trimethyl ether was obtained by Chapman, Perkin, and Robinson's method (*J.*, 1927, 3028), the yield being much improved (26.3 g.; m. p. 47°) when the following quantities were used: pyrogallol 20 g., methyl alcohol 50 c.c., methyl sulphate 45 c.c., 40% sodium hydroxide solution 90 c.c. It was converted by Graebe and Hess's method (*Annalen*, 1905, **340**, 237) into 2:6-dimethoxybenzoquinone, which gave 2:6-dimethoxyquinol on reduction with sulphurous acid. The product was treated with benzene, which removed a nitrated impurity.

When a crystal of 2:6-dimethoxyquinol is touched with 2*N*-caustic alkali on a watch-glass, an intense indigo-blue colour is produced which immediately changes to brown.

1 : 2 : 3 : 5-Tetramethoxybenzene (2.1 g.; m. p. 47°) was obtained when a mixture of 2 : 6-dimethoxyquinol (2 g.), methyl alcohol (5 c.c.), and methyl sulphate (5.2 c.c.) was treated with 40% sodium hydroxide solution (15 c.c.) in an atmosphere of hydrogen, a little heat being finally supplied.

A mixture of the tetramethoxybenzene (2 g.) and acetyl chloride (4 c.c.), cooled in water, was gradually treated with powdered aluminium chloride (2 g.). When the product became semi-solid (after 20 minutes), ice was added; 2 : 3 : 4 : 6-tetramethoxyacetophenone (2.2 g.) then crystallised in colourless needles. These were collected, digested with aqueous caustic alkali (which removed only a trace of demethylated material), and washed with water (yield, 2.1—2.2 g.). When much water was added to its concentrated methyl-alcoholic solution, the ketone separated in long fine needles (Found: C, 60.1; H, 6.4; OMe, 51.1. Calc.: C, 60.0; H, 6.6; OMe, 51.7%). The *oxime*, prepared by heating a mixture of the ketone (0.3 g.), sodium acetate (0.25 g.), hydroxylamine hydrochloride (0.25 g.), and ethyl alcohol (4 c.c.) on a water-bath for 3 hours, crystallised from dilute methyl alcohol in colourless hydrated needles, m. p. 53—54° (Found: C, 53.1; H, 7.0.  $C_{12}H_{17}O_6N, H_2O$  requires C, 52.8; H, 7.0%).

When a solution of the tetramethoxyacetophenone (1 g.) and anisaldehyde (0.7 g.) in methyl alcohol (6 c.c.) was warmed at 50—60° with 50% potassium hydroxide solution (4 g.), the methoxy-chalkone gradually crystallised. After several hours, water was added and the crystals were collected and washed with water (yield, 1.4 g.). The 2 : 3 : 4 : 6-tetramethoxyphenyl 4-methoxystyryl ketone was recrystallised from methyl alcohol (Found: C, 66.6; H, 6.0%). It then melted, alone or mixed with  $\beta$ -carthamidin pentamethyl ether, at 112° and agreed with this substance in all its properties. The absorption spectra of the two substances in  $N/5000$ -alcoholic solution, kindly photographed by Mr. Sakurai, the iron arc being used as a light source, were identical in every respect. Both showed a very wide band with its centre at about  $\lambda$  3300 Å. and another smaller band at about  $\lambda$  2700 Å. Indications of sharp narrow bands were observed in both cases in the region about  $\lambda$  3800 Å.

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