

authors' were consistent with the proposed structure IA, information available was insufficient for the structure to be considered fully established, because an alternative structure IB could not be excluded. The alternate structure IB was abandoned for the following reasons. In nuclear magnetic resonance spectrum, ketolactone IV shows octet peaks in the region of 5.92~6.87 analysed as AB parts of ABX system ( $\tau_A$ ; 6.14,  $\tau_B$ ; 6.66,  $J_{AB}$ ; 17.4 c.p.s.,  $J_{AX}$ ; 8.7 c.p.s.,  $J_{BX}$ ; 4.0 c.p.s.). Nuclear magnetic resonance spectra of IV, as well as those of its related compounds (I, II, and III), indicate that these octet peaks mentioned above originated from the two methylene protons on C-11 adjacent to the carbonyl carbon C-12, and furthermore, this methylene group is neighbored by methine function (C-9-H). Since the structure IB has been eliminated spectroscopically as shown above, sciadin, dimethylsciadinonate and sciadinone have been proved to have the structure IA, II, and III, respectively.

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### The Mechanism of the New Color Reaction of Anthrone with Furfural and Pentose

The studies on the color reaction of anthrone with carbohydrate introduced by Dreywood<sup>1)</sup> have been reported by many investigators. Sattler and Zerban,<sup>2)</sup> Shriver, Webb, and Swanson,<sup>3)</sup> and Yemm and Willis<sup>4)</sup> assumed from the results of spectrophotometrical studies that the color was due to furfural compound derived from carbohydrate by strong acid. On the other hand, Momose, *et al.*<sup>5)</sup> isolated one of the main dyes as trianthronylidenepentane from the reaction mixture of anthrone with pentose or hexose, and discussed a new reaction mechanism without the formation of furfural compound.

Recently the authors have reported in the preceding paper<sup>6)</sup> that furfural gave a specific blue color with anthrone when the reaction mixture was cooled enough to keep away from the evolution of heat. When pentose was previously heated in concentrated acid in the absence of anthrone, it also gave the same blue color with anthrone, though pentose itself gave no color without heating. As this specific color was very unstable by heat, the reaction mixture should be kept in cold. The intensity of the blue color

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- 5) T. Momose, Y. Ueda, K. Sawada, A. Sugi: *This Bulletin*, **5**, 31 (1957).
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thus formed was proportional to furfural concentration, and could be used for the determination of pentose.

In the present communication, the specific color substance was isolated and its structure was investigated.

The color substance of this reaction was separated on alumina or  $\text{CaHPO}_4$  with benzene or petr. ether as eluate, and one of the main dyes was obtained as yellow syrup I. I gave a blue color in concentrated sulfuric acid, and it seemed that I had the formula  $\text{C}_{19}\text{H}_{12}\text{O}_2$  from the data of elementary analyses. UV  $\lambda_{\text{max}}^{\text{petr. ether}}$   $m\mu$ : 320, 400. UV  $\lambda_{\text{max}}^{70\% \text{H}_2\text{SO}_4}$   $m\mu$ : 600. IR  $\text{cm}^{-1}$ :  $\nu_{\text{C}=\text{O}}^{\text{liq. film}}$  1661. Pentose also gave I in the same reaction with anthrone after it was previously heated in concentrated acid in the absence of anthrone, but another carbohydrate, hexose, methylpentose, etc., gave not I.

On the other hand, it was reported that 10-benzylidene-9-anthrone (III) was prepared by the condensation of anthrone and benzaldehyde in pyridine in the presence of piperidine.<sup>7)</sup> From the reaction mixture of anthrone and furfural in the same procedure, yellow syrup II was yielded.

I and II have the same formula  $\text{C}_{19}\text{H}_{12}\text{O}_2$  and also give a blue color in concentrated sulfuric acid respectively. The absorption spectra of I and II in the infrared and ultraviolet region are identical, and are similar to those of III. Furthermore, the infrared absorption at 740, 880, and  $1020 \text{ cm}^{-1}$  shows that I and II are furan compound.<sup>8,9)</sup>

Thus, the main color substance I formed from the new color reaction introduced by the present authors<sup>8)</sup> is considered as a new substance having the structure of 10-furfurylidene-9-anthrone. This substance is rapidly decomposed by heat, and therefore, it is presumed that there is no furfurideneanthrone in the reaction mixture of the color reaction introduced by Dreywood.<sup>1)</sup>

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