



## Studies on Kojic Acid Derivatives : Part 3. Coupling Reaction of Kojic Acid with Diazonium Salts

メタデータ	言語: eng 出版者: 公開日: 2009-08-25 キーワード (Ja): キーワード (En): 作成者: MIYAGAWA, Kinjiro, ICHIMOTO, Itsuo, TATSUMI, Chuji メールアドレス: 所属:
URL	<a href="https://doi.org/10.24729/00009528">https://doi.org/10.24729/00009528</a>

## Studies on Kojic Acid Derivatives

### Part 3. Coupling Reaction of Kojic Acid with Diazonium Salts\*

By

Kinjiro MIYAGAWA, Itsuo ICHIMOTO and Chuji TATSUMI

Department of Agricultural Chemistry, College of Agriculture

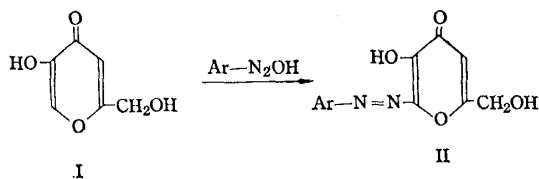
(Received August 30, 1963)

The purpose of this series was to prepare the chemically and biologically important substances from kojic acid (I) and its homologue.

In an earlier paper<sup>1)</sup> dealing with the acylation of kojic acid, it has been shown that monoacyl derivatives (7-acyl kojic acid) was only prepared from fatty acid and kojic acid in the presence of zinc chloride as a catalyst, though using of acid chloride gave diacyl derivatives (5, 7-diacyl kojic acid).

The coupling reaction of kojic acid with diazonium salts has been studied and several analogical substances of dyestuffs have been obtained by a few pionior workers<sup>2,3)</sup>. Seemingly, coupling compounds of kojic acid may be interested not only for dyestuffs but also biological properties. And it is necessary to investigate more detail information about coupling reaction.

In present experiments, kojic acid was coupled with the diazonium salts prepared from eleven aromatic amines. The validity of the structure of coupling compounds (II) was supported by infrared spectra and elementary analyses.

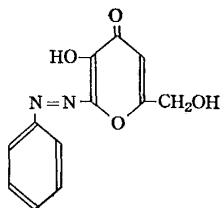


### Experimental

Aniline, *o*-chloroaniline, *m*-chloroaniline, *p*-chloroaniline, *o*-toluidine, *m*-toluidine, *p*-toluidine, *α*-naphthylamine, *β*-naphthylamine, *o*-anisidine and sulfanilic acid were used as aromatic amines. To a stirring solution of 1/60 moles of amine in 40 ml of water and 5 ml concentrated hydrochloric acid, 1/60 moles of sodium nitrite was added portionally. During the addition, reaction temperature was maintained from 0° to 5° in an ice-salt bath. After the diazo reaction was completed, the reaction mixture added to a cold solution of kojic acid in 250 ml of sodium acetate aqueous solution. The resulting colored crystal was recrystallized from methanol.

\* This paper was already reported at the meeting of Agricultural Chemical Society of Japan, Kansai branch.

## 1. Diazoaniline with kojic acid.

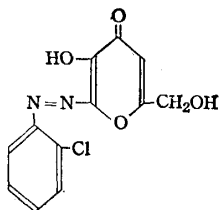


m.p. 113-114°.

Anal. Calcd. for  $C_{12}H_{10}O_4N_2$ :  
N, 11.38. Found: N, 11.29%.

Color: reddish violet.

## 2. Diazo-o-chloroaniline with kojic acid.

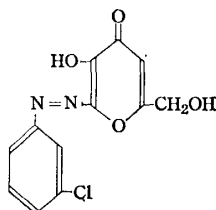


m.p. 175-177° (dec.)

Anal. Calcd. for  $C_{12}H_9O_4N_2Cl$ :  
N, 9.98. Found: N, 10.97%.

Color: reddish brown.

## 3. Diazo-m-chloroaniline with kojic acid.

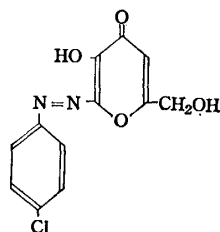


m.p. 165-167° (dec.)

Anal. Calcd. for  $C_{12}H_9O_4N_2Cl$ :  
N, 9.98. Found: N, 9.03%.

Color: pale reddish brown.

## 4. Diazo-p-chloroaniline with kojic acid.

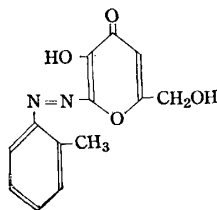


m.p. 185-186°.

Anal. Calcd. for  $C_{12}H_9O_4N_2Cl$ :  
N, 9.98. Found: N, 10.13%.

Color: red.

## 5. Diazo-o-toluidine with kojic acid.

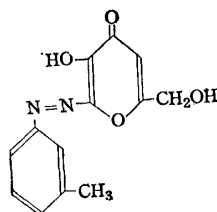


m.p. 187-189°.

Anal. Calcd. for  $C_{13}H_{12}O_4N_2$ :  
N, 10.77. Found: N, 9.98%.

Color: red.

## 6. Diazo-m-toluidine with kojic acid.

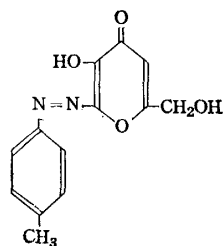


m.p. 181-182° (dec.)

Anal. Calcd. for  $C_{13}H_{12}O_4N_2$ :  
N, 10.77. Found: N, 10.35%.

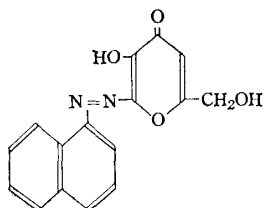
Color: red.

7. Diazo-p-toluidine with kojic acid.



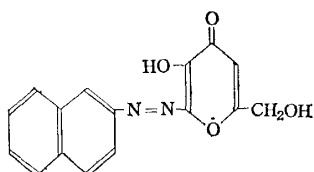
m.p. 190-191° (dec.)  
 Anal. Calcd. for  $C_{13}H_{12}O_4N_2$ :  
 N, 10.77. Found: N, 10.05%.  
 Color: blackish violet.

8. Diazo- $\alpha$ -naphthylamine with kojic acid.



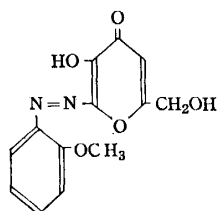
m.p. 148-149° (dec.)  
 Anal. Calcd. for  $C_{16}H_{12}O_4N_2$ :  
 N, 9.46. Found: N, 10.05%.  
 Color: greenish black.

9. Diazo- $\beta$ -naphthylamine with kojic acid.



m.p. 183-184° (dec.)  
 Anal. Calcd. for  $C_{16}H_{12}O_4N_2$ :  
 N, 9.46. Found: N, 10.56%.  
 Color: green.

10. Diazo-o-anisidine with kojic acid.

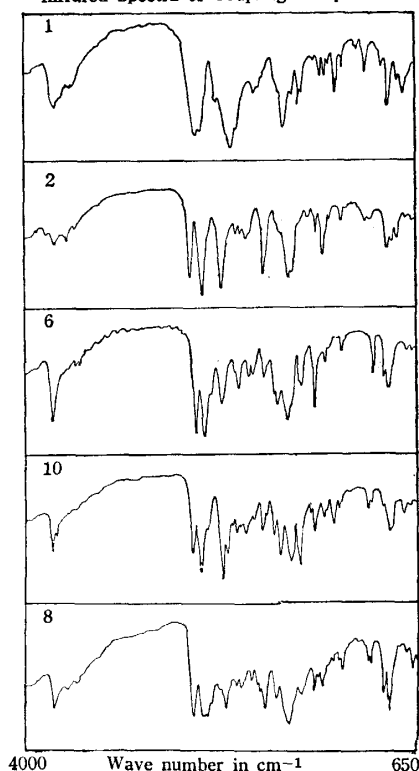


m.p. 223-225° (dec.)  
 Anal. Calcd. for  $C_{13}H_{12}O_5N_2$ :  
 N, 10.14. Found: N, 10.97%.  
 Color: black.

11. Diazo-sulfanilic acid with kojic acid.

The product decomposed by recrystallization.  
 Melting point could not be measured.

Infrared Spectra of Coupling Compounds.



### Summary

Coupling reaction of kojic acid with eleven aromatic amines were investigated. The resulting products were identified by infrared spectra and elemental analyses.

### Acknowledgement

The authors thank Mr. Y. YOSHIDA for the technical assistance.

### References

- 1) I. ICHIMOTO and C. TATSUMI, *Bull. Univ. Osaka Pref., Ser. B*, **13**, 53 (1962).
- 2) T. YABUTA, *J. Chem. Soc. Japan*, **37**, 1234 (1916).
- 3) QUILICO, C. MUSANTE, *Gazz. Chim. ital.*, **74**, 26 (1944).