

Notes

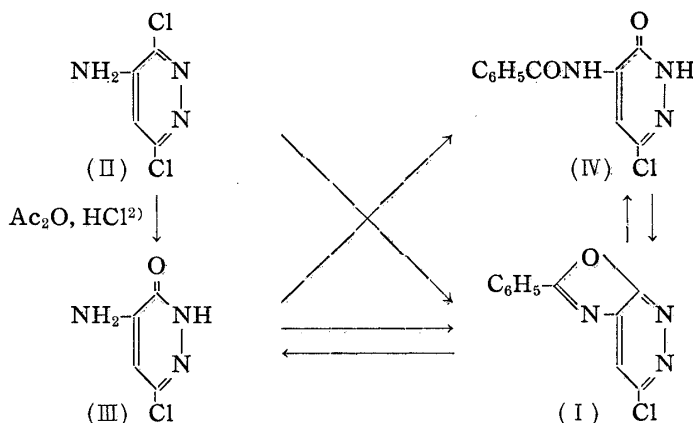
UDC 547.852.2.07

Tsukasa Kuraishi: 4,5-Disubstituted Pyridazines. VIII.¹⁾ Hydrolysis of 2-Phenyl-6-chloroöxazolo[5,4-*c*]pyridazine.

(Pharmaceutical Faculty, University of Nagasaki*¹)

Recently, the writer reported the synthesis of 2-phenyl-6-chloroöxazolo[5,4-*c*]pyridazine (I), obtained by condensation of 4-amino-3,6-dichloropyridazine (II) or 4-amino-6-chloro-3-pyridazinol (III) with benzoyl chloride.²⁾ In the process of cyclization of these pyridazine derivatives to the oxazole ring an intermediate compound (IV) having a free hydroxyl group was assumed to exist and this compound (IV) was actually isolated in the course of the reaction with nitrobenzene or pyridine as a solvent.

In this case, the final product (I) having an oxazole ring was not obtained. However, when (IV) was heated under reflux with phosphoryl chloride, a light yellow compound (I) was obtained in a good yield. The compound (IV) was also proved to be obtainable through hydrolysis of (I) with 15% hydrochloric acid, while (III) formed through hydrolysis of (I) with 15% sodium hydroxide solution.

Experimental*²

4-Benzamido-6-chloro-3-pyridazinol (IV)—i) A mixture of 0.5 g. of 4-amino-6-chloro-3-pyridazinol (III), 0.5 g. of BzCl, and 10 cc. of nitrobenzene (or pyridine) was heated under reflux for 1 hr. After removal of the solvent, the deposited crystals were collected and recrystallized from EtOH. Yield, 0.5~0.6 g. of m.p. 235°. *Anal.* Calcd. for C₁₁H₈O₂N₃Cl: C, 52.90; H, 3.20. Found: C, 53.33; H, 3.28.

ii) 0.5 g. of 2-phenyl-6-chloroöxazolo[5,4-*c*]pyridazine (I) was heated under reflux with 20 cc. of 15% HCl for 30 min. After cool, the deposited crystals were collected and recrystallized from EtOH. Yield, 0.32 g. of m.p. 234~235°. A mixed m.p. of this sample with the one obtained from (III) was not depressed.

2-Phenyl-6-chloroöxazolo[5,4-*c*]pyridazine (I)—2 g. of (IV) was heated under reflux with 10 cc. of POCl₃ in an oil bath for 1 hr. After cool, the reaction mixture was poured into 2*N* NaOH solution under ice-cooling, the deposited crystals were collected, washed with water, and recrystallized from EtOH. Yield, 0.7 g. of m.p. 209°.

*¹ Showa-machi, Nagasaki (倉石 典).

*² All m.p.s are uncorrected.

1) Part VII: This Bulletin, 6, 641(1958).

2) Part V: *Ibid.*, 6, 331(1958).

This sample showed no depression of m.p. with an authentic sample described in a previous paper.²⁾

4-Amino-6-chloro-3-pyridazinol (III)—0.5 g. of (I) was heated gently under reflux with 10 cc. of 15% NaOH solution for 30 min. After cool, the solution was acidified with AcOH and the deposited crystals were recrystallized from EtOH or water. Yield, 0.27 g. of m.p. 286°. The mixed m.p. with an authentic sample²⁾ prepared from (II) was not depressed.

Summary

1) 4-Benzamido-6-chloro-3-pyridazinol (IV) was obtained from 4-amino-6-chloro-3-pyridazinol (III) by heating with benzoyl chloride under reflux in the presence of pyridine or nitrobenzene as a solvent.

2) 2-Phenyl-6-chloroöxazolo[5,4-*c*]pyridazine (I) yielded (III) and (IV) on heating with sodium hydroxide solution and hydrochloric acid, respectively.

(Received October 26, 1959)

UDC 547.92 : 582.26

Kyosuke Tsuda*¹ und Kiyoshi Sakai*² : Untersuchungen über Steroide. XX.¹⁾ Die Sterine aus grünen Meeres-Algen.*³

(Institut für angewandte Mikrobiologie,*¹ Universität Tokio, und Takamine Forschungslaboratorium, Sankio A.G.*²)

In den vorherigen Mitteilungen²⁾ dieser Reihe haben wir Isolierung, Charakterisierung und Strukturbeweis der Sterine aus braunen sowie aus roten Meeres-Algen beschrieben. Der aus diesen Untersuchungen resultierende Schluss, dass die beiden Algen-Stämme sich in charakteristischer Weise hinsichtlich des Sterin-Bestandteils unterscheiden, interessierte uns für das in grünen Meeres-Algen enthaltene Sterin.

Die neun verschiedenen Arten von grünen Meeres-Algen wurden einst durch Carter, *et al.*³⁾ betreffs des Sterin-Bestandteils untersucht. Von diesen Autoren wurde gezeigt, dass die geprüften Grünalgen ausnahmslos das β -Sitosterin*⁴ enthielten und dass zwei Arten darunter das Fukosterin*⁴ als das Begleitsterin gaben.

In der vorliegenden Arbeit berichten wir über die Sterin-Bestandteile der grünen Meeres-Algen, die an der Küste Japans gesammelt worden sind.

Untersuchung über den unverseifbaren Anteil des Benzol-Extraktes von *Monostroma nitidum* WITTROCK*⁵ (Monostromaceae)

Die Extraktion und die darauffolgende Verseifung geschahen wie früher beschrie-

*¹ Yayoi-cho, Bunkyo-ku, Tokio (津田恭介).

*² Nishishinagawa, Shinagawa-ku, Tokio (酒井 淨).

*³ Vorgetragen bei der Jahresversammlung von Japanischer Pharmazeutischer Gesellschaft in Tokio, April, 1960. Vgl. Referatenband, 221(1960).

*⁴ Betreffs der Identifizierung dieser beiden Sterine wurden nur die physikalischen Konstanten des freien Sterins bzw. Sterylacetates mit den bereits in der Literatur vorhandenen Angaben verglichen.

*⁵ Diese Alge heisst "Hitoyegusa" auf Japanisch. Sie wurde im März und April, 1958, in der Bai von Hamana (Aichi-ken) gesammelt.

1) XIX. Mitt. Y. Kishida : Dieses Bulletin, 8, 357(1960).

2) K. Tsuda, R. Hayatsu, Y. Kishida, S. Akagi : J. Am. Chem. Soc., 80, 921(1958); R. Hayatsu : Dieses Bulletin, 5, 452(1957); K. Tsuda, S. Akagi, Y. Kishida : Science, 126, 927(1957); Dieses Bulletin, 6, 101(1958); K. Tsuda, S. Akagi, Y. Kishida, K. Sakai : Dieses Bulletin, 6, 724(1958).

3) P. W. Carter, I. M. Heilbron, B. Lythgoe : Proc. Roy. Soc. (London), B 128, 82(1939).