C, 53.05; H, 5.3; N, 14.7. Found: C, 53.05; H, 5.1; N, 14.6.

Picrolonate of (III): Faint yellow plates (from EtOH), m.p. 230°(decomp.). *Anal.* Calcd. for $C_{25}H_{30}O_6N_6$: C, 58.8; H, 5.9; N, 16.5. Found: C, 58.7; H, 5.8; N, 16.5.

**Summary**

α-Bromo-α-methyl-δ-phthalimidovaler-*p*-anisidide (VIII) was fused with aluminum chloride according to Stollé to give 5-methoxy-1,3-dimethyl-3-(γ-phthalimidopropyl)oxindole (IX) after methylation. Phthalimido group could be readily removed from this compound by the standard method, furnishing 3-(γ-aminopropyl)oxindole derivative (X), which was then monomethylated to (XI). This compound could also be prepared advantageously by reducing 5-methoxy-1,3-dimethyl-3-(β-cyanoethyl)oxindole (XII) catalytically in the presence of methylamine. On being reduced with sodium in boiling ethanol the latter gave rise to a single *dl*-homoesermethole (III) in a fair yield, no isomeric base being detected in the reduction product.

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*UDC 547.68.02*

## 35. Osamu Tanaka: Metabolic Products of Fungi. XIV.[1] The Structure of Skyrin. (3). On Pseudoskyrin.

(*Pharmaceutical Institute, Medical Faculty, University of Tokyo**)

The structure of skyrin, an orange-red coloring matter which was isolated from various fungi,[2~6] was established as diemodin-(8,8′)(I) by the synthesis of its 2,2′-dimethyl ether (II).[4,5] However, a peculiar nature of skyrin on which a short discussion was given in the previous paper[4] has remained for further studies.

Howard and Raistrick[2] described that on treatment with alcoholic sulfuric acid, hexaacetylskyrin was converted into yellow crystalline dialkylskyrin, whose properties, as were pointed out earlier,[4] especially the instability of these alkoxyl groups to the action of cold aq. alkali, were not explained by the ordinary β-alkyl ether of polyhydroxybianthraquinone-(1,1′). It was found that on the action of diazomethane, skyrin yielded a genuine 2,2′-dimethyl ether (II), and it was suggested that the alkyl ether prepared by Howard and Raistrick would be the product of isomerization, for which a structural formula (VI) and (IX) was proposed.[4]

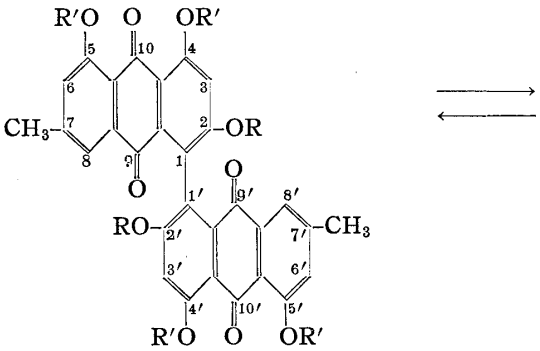
Some further evidences for the isomerization of skyrin to establish the correctness of the proposed structure of dialkylpseudoskyrin have now been accumulated.

The isomerized alkyl ether of skyrin, which was named dialkylpseudoskyrin, was prepared directly from skyrin by the action of alcoholic sulfuric acid, and also by refluxing crude skyrin in alcohol. On boiling in glacial acetic acid for a short time, dialkylpseudoskyrin regenerated skyrin.

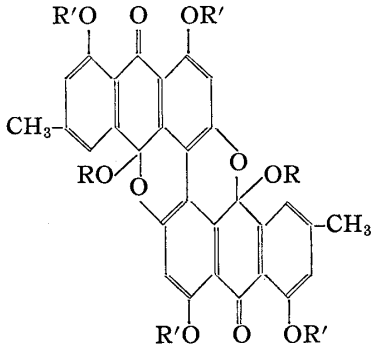
Dialkylpseudoskyrin gave tetraacetate (VII) (its infrared spectrum showed a phenolic acetate C=O band at 1772 $cm^{-1}$ in chlorofrom), and tetrakis(ethyl carbonate) (VIII, XI). These derivatives as well as dialkylpseudoskyrin itself were readily hydrolyzed

* Hongo, Tokyo (田中 治).

1) Part XIII. S. Shibata, M. Takido, M. Ohta, T. Kurosu: This Bulletin, **5**, 573(1957).
2) B.H. Howard, H. Raistrick: Biochem. J., **56**, 56(1954).
3) J. Breen, J.C. Dacre, H. Raistrick, G. Smith: *Ibid.*, **60**, 618(1955).
4) S. Shibata, O. Tanaka, I. Kitagawa: This Bulletin, **3**, 278(1955); **4**, 147(1956).
5) O. Tanaka, C. Kaneko: *Ibid.*, **3**, 284(1955).
6) S. Shibata, J. Shoji, A. Ohta, M. Watanabe: *Ibid.*, **5**, 380(1957).

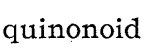


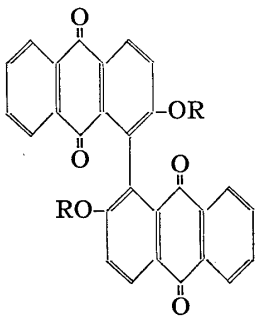
(I) R=R′=H
(II) R=$CH_3$, R′=H
(III) R=$COCH_3$, R′=H
(IV) R=$COCH_3$, R′=$CH_3$
($\alpha$: 4,4′,5,5′,8,8′
$\beta$: 2,2′,3,3′,6,6′,7,7′)



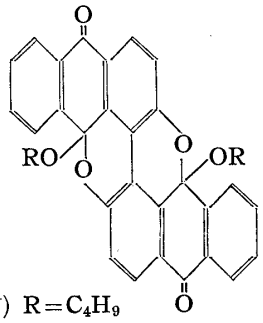
(V) R=R′=H
(VI) R=$CH_3$, R′=H
(VII) R=$CH_3$, R′=$COCH_3$
(VIII) R=$CH_3$, R′=$COOC_2H_5$
(IX) R=$C_2H_5$, R′=H
(X) R=$C_4H_9$, R′=H
(XI) R=$C_4H_9$, R′=$COOC_2H_5$

with alkali to regenerate skyrin. These results indicated that dialkylpseudoskyrin possesses four phenolic hydroxyls which are subjected to acetylation or ethoxycarbonylation.

2,2′-Diacetoxybianthraquinone-(1,1′) (XIII) could be converted into the pseudo-type dibutyl ether (XIV) by the action of butanolic sulfuric acid. The resulting pseudo-dibutyl ether showed some resistance to alkaline hydrolysis, whereas it regenerated 2,2′-dihydroxybianthraquinone-(1,1′) (XII) on boiling with glacial acetic acid. The presence of a quinonoid structure  in this compound (XIV) was excluded, since it did not give vat dye on the action of sodium dithionite in warm aq. alkali.



(XII) R=H,
(XIII) R=$COCH_3$



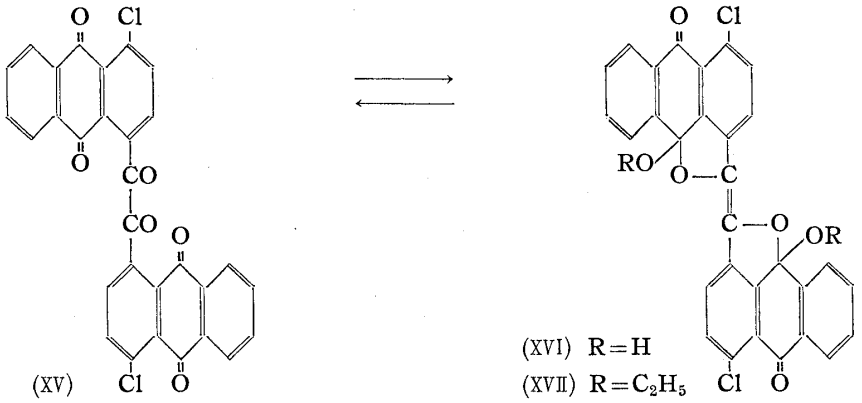
(XIV) R=$C_4H_9$

The pseudoisomerization was also observed in 2,2′-diacetyl-4,4′,5,5′-tetramethylskyrin (IV) prepared from 2,2′-diacetylskyrin (III),[7] whereas the genuine 2,2′-dimethyl ether (II) of skyrin, hexamethylskyrin, 4,4′-dihydroxy-2,2′-dimethoxybianthraquinone-(1,1′), emodin, and xanthopurpurin gave no evidence of such isomerization. From these results, the free hydroxyl group in the 2-position of bianthraquinone-(1,1′) was proved to be indispensable for the pseudo-ring formation.

The infrared spectrum of dimethylpseudoskyrin showed a chelated C=O band at 1648 $cm^{-1}$ but not non-chelated C=O and O-H bands (in Nujol), while its tetraacetate (VII) gave only a non-chelated C=O band at 1674 $cm^{-1}$ (in Nujol). Thus the participation of the ketone in the 9-position of skyrin structure for the isomerization was evident, while the ketone in the 10-position remained indifferent.

As an example of the ketal ring formation of anthraquinone derivatives, it should be noted that on treatment with conc. sulfuric acid, the compound (XV) gave an unstable sulfate of the compound (XVI) which yielded with ethanol an easily hydrolyzable diethyl

7) The stability of the pseudo-form seemed to be somewhat affected by substituents in the ring.




ether (XVII).[8]

Consequently, all the evidences provided in the present study agree quite sufficiently with the proposed structure for dialkylpseudoskyrin (VI, IX, and X), and the novel isomerization reaction of 2,2′-diacetoxybianthraquinone-(1,1′) (XIII) has been established.

On treatment with conc. sulfuric acid under cooling for a few minutes, skyrin itself is isomerized into pseudoskyrin (V), the ultraviolet spectrum of which was fairly well superimposable with that of dimethylpseudoskyrin (VI) (Fig. 1). This fact indicated that

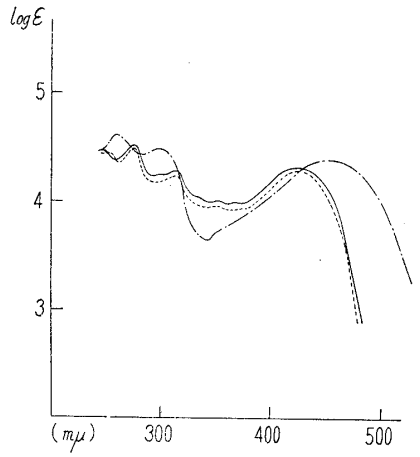



Fig. 1. Ultraviolet Spectra (in $CHCl_3$)

—·—·— Skyrin (I)
——— Pseudoskyrin (V)
---------- Dimethylpseudoskyrin (XI)

the emerald green coloration of skyrin and its acetate[9] with conc. sulfuric acid is a characteristic reaction showing the pseudo-isomerization. Tetraacetylbirubiadin-(4,4′) (XXII) prepared as shown in Chart 1, as well as oxyskyrin[1] showed similar coloration

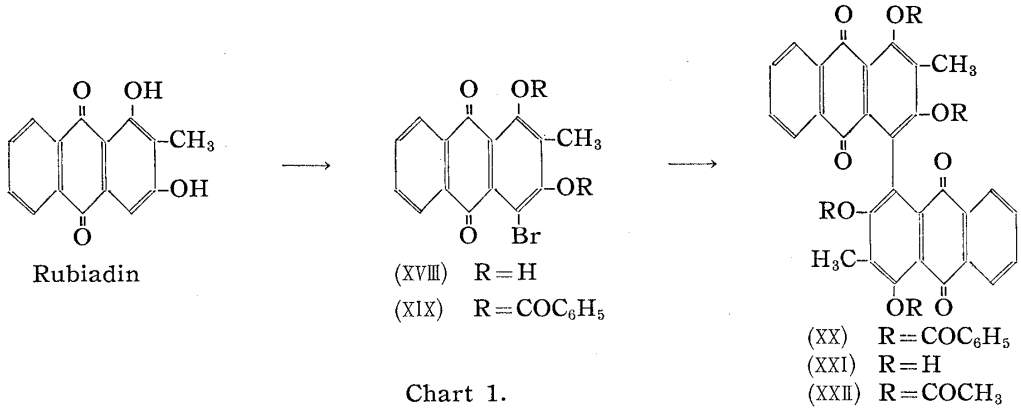



Chart 1.

8) R. Scholl, H-D. Wallenstein : Ber. **69**, 503(1936); R. Scholl, J. Donat, S. Hass : *Ibid.*, **68**, 2063 (1935).

9) The acetoxyl group of anthraquinone derivatives is easily hydrolyzed with cold conc. sulfuric acid to a free hydroxyl.

with conc. sulfuric acid, while 2,2′-dihydroxybianthraquinone-(1,1′) (XII), 2,2′-diacetyl-4,4′,5,5′-tetramethylskyrin (IV), and their pseudo-forms gave no green coloration.

Therefore, it may be concluded that the green coloration with conc. sulfuric acid is exhibited by the pseudo-isomerization of bianthraquinone-(1,1′) possessing free hydroxyls in the 2- and 4-positions.

The author wishes to express his gratitude to Prof. S. Shibata for his kind advice and encouragement through the course of this work. The microanalyses were carried out by the members of Microanalytical Laboratories of this Institute, the Institute of Applied Microbiology, and the Institute for Infectious Diseases, University of Tokyo, to whom thanks are due. The author is indebted to Mr. K. Tanikawa of this laboratory for the measurement of infrared spectra. This work was supported partly by a Grant in Aid for Scientific Research from the Ministry of Education, to which the author is also grateful.

## Experimental[11]

**Dimethylpseudoskyrin (VI)**—A suspension of skyrin (I) in MeOH containing $H_2SO_4$(3%) was refluxed for about 8 hrs. During the reaction, skyrin was gradually converted into greenish yellow crystals which were collected, washed with MeOH, and recrystallized from dioxane to dimethylpseudoskyrin as yellow crystals, m.p. >360°. Its identity was confirmed by the comparison of its infrared spectra with Howard and Raistrick's dimethylskyrin, obtained from hexaacetylskyrin by refluxing in MeOH-$H_2SO_4$ (*Anal.* Calcd. for $C_{32}H_{22}O_{10}$: C, 67.8; H, 3.9; 2 $OCH_3$, 11.0. Found: C, 67.3; H, 4.1; $OCH_3$, 11.1).[2]

It dissolves in cold aq. NaOH, from which skyrin is recovered by acidification after standing for a few mins. at a room temperature, and skyrin is also regenerated from this substance by refluxing in glacial AcOH for a short time. It dissolves in conc. $H_2SO_4$ with green color, and is slightly soluble in $CHCl_3$, dioxane, and pyridine, but almost insoluble in other ordinary organic solvents and aq. $Na_2CO_3$ solution.

**Dimethyltetraacetylpseudoskyrin (VII)**—Dimethylpseudoskyrin (VI) (0.1 g.) was acetylated with $(AcO)_2O$ (3 cc.) in cold anhyd. pyridine (20 cc.) with stirring. After standing overnight, the reaction mixture was poured on ice and the precipitate was recrystallized from $CHCl_3$-MeOH mixture to dimethyltetraacetylpseudoskyrin as pale yellow needles, darkening above ca. 230°. It dissolves in conc. $H_2SO_4$ with green color. *Anal.* Calcd. for $C_{40}H_{30}O_{14}\cdot CH_3OH$: C, 64.23; H, 4.44; 4 $CH_3CO$, 22.4. Found: C, 64.02, 64.24; H, 4.35, 4.43; $CH_3CO$, 21.6. *Anal.* Calcd. for $C_{40}H_{30}O_{14}$: C, 65.38; H, 4.08; 2 $OCH_3$, 8.5. Found (dried at 140° for 4 hrs. *in vacuo*): C, 65.04; H, 4.39; $CH_3O$, 8.6.

When the acetylation with $Ac_2O$ and pyridine was carried out at a very low temperture or with an insufficient amount of pyridine yellow, less soluble by-product sometimes formed, which seemed to be a partly acetylated dimethylpseudoskyrin, since further acetylation of this substance gave the foregoing tetraacetate.

**Dimethylpseudoskyrin Tetrakis(ethyl carbonate) (VIII)**—ClCOOEt (2 cc.) was gradually added to a suspension of dimethylpseudoskyrin (VI) (0.2 g.) in anhyd. pyridine (20 cc.) under stirring and ice-cooling. After standing overnight, the reaction mixture was poured on ice. The precipitate, on recrystallization from acetone-MeOH mixture, gave dimethylpseudoskyrin tetrakis(ethyl carbonate) in white needles, m.p. 208~210°(decomp.). *Anal.* Calcd. for $C_{44}H_{38}O_{18}$: C, 61.82; H, 4.45. Found: C, 61.58; H, 4.55.

**Dibutylpseudoskyrin Tetrakis(ethyl carbonate) (XI)**—A suspension of skyrin (I) in BuOH containing $H_2SO_4$ (3%) was warmed on a water bath for a few hrs. The resulting greenish yellow crystals (dibutylpseudoskyrin (X)), which show properties similar to dimethylpseudoskyrin, in conc. $H_2SO_4$ and aq. NaOH, were ethoxycarbonylated with ClCOOEt in cold anhyd. pyridine, to give dibutylpseudoskyrin tetrakis(ethyl carbonate) in white needles (from BuOH), decomposing at 140~200°. *Anal.* Calcd. for $C_{50}H_{50}O_{18}$: C, 63.96; H, 5.33. Found: C, 63.91; H, 5.63.

**Pseudoskyrin (V)**—Skyrin (I) was dissolved in cold conc. $H_2SO_4$ and kept at room temperature for a few mins. (longer standing of over 10 mins. gave only a green polymerized substance). The resulting green solution was poured on ice and the green precipitate was repeatedly extracted with boiling $CHCl_3$. The solvent was evaporated and the residue was treated with acetone to remove skyrin which regenerated during the extraction. Recrystallization of the residue from pyridine gave greenish yellow crystalline powder, m.p. >360°. Its U.V. spectrum in $CHCl_3$ (Fig. 1) and its behavior in conc. $H_2SO_4$, aq. NaOH, and boiling glacial AcOH are almost identical to those of dimethylskyrin. Although this substance was not obtained in the analytically pure state, it is doubtless that the product is pseudoskyrin (V).

11) Owing to the remarkable sensibilty againist alkali contamination in the capillary glass, some of the compounds often showed indefinite depression of melting or decomposition point.

**Dibutylpseudo-2,2′-dihydroxybianthraquinone-(1,1′) (XIV)**—A solution of 2,2′-diacetoxybianthraquinone-(1,1′) (XIII) in BuOH containing conc. $H_2SO_4$ (3%) was refluxed for a few hrs. Crude dibutylpseudo-2,2′-dihydroxybianthraquinone-(1,1′) deposited from the cooled solution, which was recrystallized from BuOH to white prisms, m.p. 194~196°. *Anal.* Calcd. for $C_{36}H_{30}O_6$ : C, 77.42; H, 5.37. Found: C, 77.20; H, 5.42.

It is soluble in conc. $H_2SO_4$ to give a brownish red solution but insoluble in a warm alkaline $Na_2S_2O_4$ solution. It is also insoluble in aq. or ethanolic alkali, even on warming for a long time, but regenerates 2,2′-dihydroxybianthraquinone-(1,1′) (XII) on refluxing in glacial AcOH for a short time. Its I.R. spectrum in $CHCl_3$ shows a C=O band at 1670 $cm^{-1}$.

**2,2′-Diacetylskyrin (III)**—The pyridine adduct of skyrin (0.5 g.), $Ac_2O$ (15 cc.), and anhyd. NaOAc (0.4 g.) were reacted at a room temperature with stirring and left overnight. The orange crystals that deposited were chromatographed in benzene on activated $CaHPO_4$ and recrystallized from glacial AcOH to 2,2′-diacetylskyrin as orange needles, decomposing over ca 270°. It is insoluble in cold aq. $Na_2CO_3$ but soluble in cold aq. NaOH with red color. *Anal.* Calcd. for $C_{34}H_{22}O_{12}$ : C, 65.59; H, 3.53. Found : C, 65.27; H, 3.60. U.V. $\lambda_{max}^{CHCl_3}$ mμ (log ε) : 258 (4.68), 445 (4.45); inflexion 280~290 mμ (log ε 4.35). This spectrum is almost similar to that of dianhydrorugulosin[11] and its coloration with conc. $H_2SO_4$ is identical with that of skyrin. Its I.R. spectrum shows a phenolic acetate C=O band at 1770 $cm^{-1}$, free C=O band at 1675 $cm^{-1}$, and chelated C=O band at 1625 $cm^{-1}$ (in Nujol).

**2,2′-Diacetyl-4,4′,5,5′-tetramethylskyrin (IV)**—2,2′-Diacetylskyrin (III) (0.3 g.), $Ag_2O$ (1.1 g.) (added in portions), and MeI (18 cc.) were refluxed for 35 hrs. The solution was filtered and everporated. Treatment of the residue with benzene gave yellow crystals which were recrystallized from glacial AcOH to yellow prisms, melting at ca 150~180° and remelting at ca. 260~270°(decomp.). *Anal.* Calcd. for $C_{38}H_{30}O_{12}\cdot H_2O$ : C, 65.52; H, 4.59. Found : C, 65.73; H, 4.68. *Anal.* Calcd. for $C_{38}H_{30}O_{12}$ : C, 67.26; H, 4.72. Found (dried at 140° for 4 hrs. *in vacuo*) : C, 67.24; H, 4.59.

2,2′-Diacetyl-4,4′,5,5′-tetramethylskyrin so obtained is insoluble in cold aq. NaOH and gives a brownish red coloration with conc. $H_2SO_4$ which does not become green on standing. Its I.R. spectrum has absorption bands at 1760 (phenolic acetate C=O) and 1675 $cm^{-1}$ (free C=O) but does not show any chelated C=O band in the region of 1620~1640 $cm^{-1}$ (in Nujol). U.V. $\lambda_{max}^{CHCl_3}$ mμ (log ε) : 264 (4.68), 394 (4.18). This U.V. spectrum is almost similar to that of tetramethyldianhydrorugulosin[11] ($\lambda_{max}^{CHCl_3}$ mμ: (log ε) : 264 (4.56), 394 (4.02)).

Hydrolysis of this compound with hot aq. NaOH and acidification with dil. HCl gave orange-yellow precipitate which changed to greenish yellow substance on warming in dil. HCl or on long standing. This substance showed U.V. absorption similar to that of hexamethylpseudoskyrin described below. Treatment of this orange-yellow precipitate with ordinary organic solvent such as acetone, $CHCl_3$, or dioxane, affords a mixture of yellow and orange powder giving two spots on paper chromatography using the upper layer of a mixture (7:7:1) of acetone-petr. benzine (b.p. 60~70°)-water as a developing solvent. One of these spots exhibited a red color with $NH_3$, and the other showed no change of color with the same reagent. Owing to easy interconvertibility, the two substances could not be isolated in pure state.

**Hexamethylpseudoskyrin** (?)—2,2′-Diacetyl-4,4′,5,5′-tetramethylskyrin (IV) was refluxed for 4 hrs. in MeOH containing $H_2SO_4$ (3%). Yellow crystals deposited on cooling, which were clearly distinguishable from genuine hexamethylskyrin and gave a brown color with conc. $H_2SO_4$. It is insoluble in aq. NaOH even on heating for a long time. This substance could not be obtained in the analytically pure state, owing to its partial alteration into an alkali-soluble compound during recrystallization from dioxane, or on standing for a few days.

**4,5-Dimethylemodin (1,8-Dimethoxy-3-hydroxy-6-methylanthraquinone)**—Reductive cleavage of 2,2′-diacetyl-4,4′,5,5′-teramethylskyrin (IV) with $Na_2S_2O_4$ in alkaline solution after hydrolysis with hot aq. NaOH gave 4,5-dimethylemodin, which was recrystallized from MeOH to orange needles, m.p. ca. 275~280°(decomp.), giving trimethylemodin on methylation with diazomethane. *Anal.* Calcd. for $C_{17}H_{14}O_5$ : C, 68.45; H, 4.70. Found : C, 68.37; H, 5.09. It dissolves in aq. $Na_2CO_3$ with red color. Its infrared spectrum was discussed in the previous report.[12]

**4-Bromodibenzoylrubiadin (XIX)**—A solution of $Br_2$ (0.75 g.) in glacial AcOH (2 cc.) was gradually added to a suspension of rubiadin[13] (0.63 g.) in the same solvent (25 cc.) containing NaOAc (0.6 g.) under vigorous stirring at a room temperature. Then the mixture was warmed on a water bath for 1 hr. and allowed to cool to a room temperature. The product (0.63 g.) that separated was recrystallized from glacial AcOH to orange needles (4-bromorubiadin (XVIII)), m.p. 203~205°. This compound, benzoylated with BzCl in anhyd. pyridine, formed 4-bromodibenzoylrubiadin (XIX) as yellow needles, m.p.

11) S. Shibata, T. Murakami, I. Kitagawa, T. Kishi : This Bulletin, **4**, 111(1956).
12) O. Tanaka : *Ibid.*, **6**, 18(1958).
13) Rubiadin was prepared from 2-aminoanthraquinone (cf. B.S. Joshi, N. Parkash, K. Venkataraman : J. Sci. Ind. Research (India), **14B**, 87(1955)).

242～244°(from glacial AcOH). *Anal.* Calcd. for $C_{29}H_{17}O_6Br$ : C, 64.33; H, 3.14. Found : C, 64.61; H, 3.39.

**Tetraacetylbirubiadin-(4,4′) (XXII)**—4-Bromodibenzoylrubiadin (XIX) (0.9 g.), activated Cu powder (1.0 g.), and naphthalene (3.0 g.) were refluxed for 3 hrs. at 220～230°. After removal of naphthalene by extraction with hexane, the mixture was successively extracted with $CHCl_3$. The solution was filtered and evaporated. Hydrolysis of the residue with boiling ethanolic NaOH, followed by acidification with dil. HCl, gave an orange precipitate which was taken up in ether. The ethereal solution was shaken with aq. $Na_2CO_3$ and the $Na_2CO_3$ layer was reacidified to give orange precipitate which was purified by chromatography on activated $CaHPO_4$ and acetylated with $Ac_2O$ in anhyd. pyridine. The product, on recrystallization from an acetone-EtOH mixture gave tetraacetylbirubiadin-(4,4′) (XXII) as yellow needles, m.p. ca. 280°(decomp.). *Anal.* Calcd. for $C_{38}H_{26}O_{12}$ : C, 67.65; H, 3.85. Found: C. 67.41; H, 3.75.

It gives a red coloration with conc. $H_2SO_4$ which changes to an emerald green color within a few seconds and its U.V. spectrum ($\lambda_{max}^{CHCl_3}$ mμ (log ε) : 258 (4.92), 240 (4.01)) is almost identical with that of 2,2′-diacetoxybianthraquinone-(1,1′). I.R. 1765 $cm^{-1}$ (phenolic acetate C=O), 1672 $cm^{-1}$ (C=O) (in Nujol).

## Summary

The structures of dialkylpseudoskyrin and its related compounds were discussed and it was shown that all the evidences provided agreed quite sufficiently with the structure proposed in the previous paper.[4] The mechanism of the coloration of skyrin with conc. sulfuric acid was also discussed using some model compounds (tetraacetylbirubiadin-(4,4′), etc.).

(Received December 5, 1957)

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*UDC 547.755.071*

## 36. Eiji Ochiai und Masayuki Ishikawa : Synthese von Derivaten der Cinchona-Alkaloide. XXVII.[1] Ableitung von Dihydrocinchonamin aus Cinchonin.

(*Pharmazeutisches Institut, Medizin. Fakultät, Universität Tokyo**)

In Fortsetzung der Versuche zur Überführung der Alkaloide der Chinin-Reihe in diejenigen der Cinchonamin-Reihe haben wir unternommen, Dihydrocinchonin ganz analog wie beim Dihydrochinin[1] nach unten angegebenen Reaktionsstufen in eine Verbindung überzuführen, die dem Dihydrocinchonamin oder seinem Stereoisomer auf der 8-Stellung der Chinuclidinkette entspricht.

Die Reaktionen verliefen beinahe wie erwartet und wir konnten sie zu einer Verbindung (XI) ableiten, die wirklich mit dem Dihydrocinchonamin identifiziert wurde.

Die Oxydation von Dihydorcinchonin (I) mit Wasserstoffperoxyd und Eisessig ergab ein Mono-N-oxyd (Prismen vom Schmp. 237～238.5°) (II) mit der Ausbeute von 40～45% der Theorie. Sein UV-Spektrum, welches mit demjenigen des Dihydrocinchonins in der Fig. 1 vergleichend gezeigt wurde, zeigt, dass das letztere ein Chinolin-N-oxyd-Derivat ist.[2] (II) ist also Dihydrocinchonin-*ar*-N-oxyd. Sehr merkwürdig ist, dass hierbei nur ein *ar*-Mono-N-oxyd entstanden ist, weil ganz analoge Oxydation von Chinin bzw. Dihydrochinin sein N,N′-Dioxyd ergab, welches erst durch Reduktion mit schwefliger Säure in *ar*-Mono-N-oxyd übergeführt wurde.[3] Es ist umso merkwürdiger,

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* Hongo, Tokio (落合英二, 石川正幸).

1) XXVI. Mitt. M. Ishikawa : Dieses Bulletin, **6**, 71(1958).

2) vgl. dazu H. Hirayama, T. Kubota : Yakugaku Zasshi, **72**, 1025(1952); M. Colonna : Boll. sci. Fac. chim. ind. Bologna, **15**, 1(1957).

3) E. Ochiai, G. Kobayashi, J. Hasegawa : Yakugaku Zasshi, **67**, 101(1947).