Table II. Δ Log RRT of Converted Functional Group of Corticosteroids

Converted functional group	Compound No.	Δ Log RRT
21-OTMSi	1～P[a)]	0.206
17α-OTMSi	2～1	0.048
	5～4	0.051
11=O	3～2	0.110
21-OTMSi ⟶ 21-OAc	9～5	0.070
	8～3	0.100

a) progesterone

Utilization of the Δ log RRT value would have the following advantages : a) prediction of the RRT values of given corticosteroids, and b) identification of corticoids from their RRT values.

Making use of this general procedure for protecting the side chains of corticosteroids, further investigations concerning the analysis of other synthetic steroids and corticosteroids contained in biological materials are in progress.

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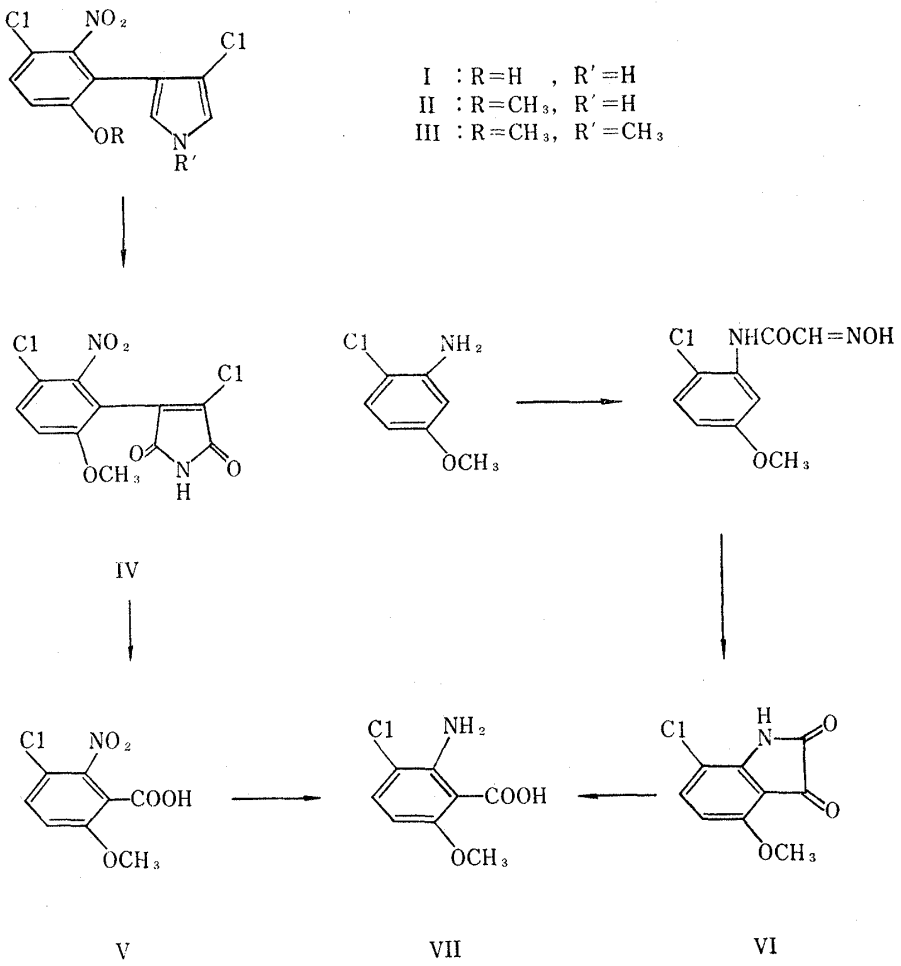
Oxypyrrolnitrin : A Metabolite of *Pseudomonas*

In studies on the metabolites of *Pseudomonas*, 3-chloro-4-(2-nitro-3-chlorophenyl)-pyrrole[1] and 2,3-dichloro-4-(2-nitrophenyl)pyrrole[2] were found to exist. Further investigations showed a coexistence of oxypyrrolnitrin in the same cultural broth. The existence of these metabolites are easily recognized by the characteristic color reaction using Ehrlich reagent.

The acetone extract of this bacterial cell was purified by column chromatography using silica gel and benzene-chloroform, and pale yellow rhombic crystals were obtained by recrystallization from ether-hexane solution; (I), m.p. 215～216°(dec.), mol. wt. 273 by mass spectrometry, $C_{10}H_6O_3N_2Cl_2$ (*Anal.* Calcd. : C, 43.99; H, 2.22; N, 10.26. Found : C, 43.93; H, 2.18; N, 10.26), UV λ_{max}^{EtOH} mμ (log ε) : 290 (3.54). The infrared spectrum of this substance showed the presence of the following functional groups; -NH (3300 cm^{-1}), -OH (3475, 1193 cm^{-1}) and $-NO_2$ (1530, 1365 cm^{-1}).

1) Pyrrolnitrin : K. Arima, H. Imanaka, M. Kousaka, A. Fukuta, G. Tamura : Agr. Biol. Chem., **28**, 575 (1964).
2) Isopyrrolnitrin : M. Hashimoto, K. Hattori : Bull. Chem. Soc. Jap., **39**, 410 (1966).



Methylation of I with diazomethane produced O-methyl derivative (II), m.p. 152~154°, $C_{11}H_8O_3N_2Cl_2$ (*Anal.* Calcd.: C, 46.06; H, 2.81; N, 9.76. Found: C, 46.31; H, 3.04; N, 9.99). Further methylation with dimethylsulfate gave N,O-dimethyl derivative (III), m.p. 135~137°, in which the characteristic infrared absorption bands of the -NH and the -OH groups disappeared. When II was oxidized with chromium trioxide in acetic acid, a compound (IV) was obtained; m.p. 260~275° (dec.), $C_{11}H_6O_5N_2Cl_2$ (*Anal.* Calcd.: C, 41.64; H, 1.91; N, 8.83. Found : C, 41.49; H, 2.14; N, 8.84). It was easily understood from its infrared absorption bands (1792, 1748 cm^{-1}), that this oxidation product (IV) had a maleinimide structure. By more rigorous oxidation with potassium permanganate in acetic acid, IV was degradated to an aromatic carboxylic acid (V), m.p. 196~202° (dec.), $C_8H_6O_5NCl$ (*Anal.* Calcd.: C, 41.48; H, 2.61; N, 6.05. Found: C, 41.29; H, 2.41; N, 6.12). Analysis of information about this carboxylic acid revealed the presence of two possible structures, and one of them was synthesized as follows.

4-Methoxy-7-chloroisatin (VI) was prepared from 2-chloro-4-methoxyaniline by usual procedure;[3] (VI), m.p. 237~238° (dec.), $C_9H_6O_3NCl$ (*Anal.* Calcd. : C, 51.09; H, 2.86; N, 6.64. Found : C, 51.36; H, 2.98; N, 6.93). Oxidation of VI with hydrogen peroxide in alkaline solution gave 2-amino-3-chloro-6-methoxybenzoic acid (VII), m.p. 125~126°, $C_8H_8O_3NCl$ (*Anal.* Calcd. : C, 47.66; H, 4.00; N, 6.95. Found : C, 47.70; H, 4.01; N, 6.84).

Because of some difficulty of purification, the carboxylic acid (V) derived from the natural metabolite (I) was converted to VII by catalytic reduction, and comparison of thus obtained VII with that prepared by synthetic material gave identity.

3) W.C. Sumpter, W.F. Jones : J. Am. Chem. Soc., **65**, 1802 (1943); Org. Synth., coll. vol. **1**, p. 327.

Hence the structure of oxypyrrolnitrin (I) was established as 3-chloro-4-(2-nitro-3-chloro-6-hydroxyphenyl)pyrrole. Examination on the possibility of artificial formation of I from pyrrolnitrin also showed such chemical oxidizing agents as oxygen and hydrogen peroxide to be useless for this transformation.

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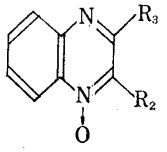
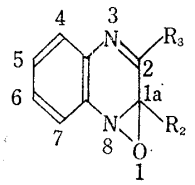
Three-membered Ring System with Two Hetero Atoms. VI.*1 Photochemical Synthesis of 1a*H*-Oxazirino[2,3-*a*]quinoxaline Derivatives and Their Thermal Reactions.

We have extended our studies on the photochemical reactions of quinoline,[1~3] isoquinoline[1,3] and pyridine N-oxides[4] to quinoxaline 1-oxides (Ia, b, c), and we now report the synthesis of two novel heterocyclic compounds, IIa and IIb, having the so far unknown 1a*H*-oxazirino[2,3-*a*]quinoxaline ring system, together with some of their thermal reactions.



I



II

(a) $R_2=R_3=C_6H_5$
(b) $R_2=C_6H_5$, $R_3=H$
(c) $R_2=H$, $R_3=C_6H_5$

Irradiation of 2,3-diphenylquinoxaline 1-oxide (Ia)[5] in benzene was carried out as described in our previous paper.[3] After the irradiation, the irradiated mixture was concentrated under reduced pressure, and the portion soluble in hexane-ether (1:1 v/v) was chromatographed over silica gel. Only one compound, IIa, m.p. 98~99°, $C_{20}H_{14}ON_2$,*3 [UV λ_{max}^{EtOH} mμ (log ε): 262 (4.58), 326 (3.86); IR ν_{max}^{KBr} cm^{-1}: 1667s, 1330w, 1284w, 1230w, 1204m, 755m, 689m], was obtained in 60~70% yield as calculated from the N-oxide consumed. The portion insoluble in the above solvent was directly recrystallized from

*1 Part V. C. Kaneko, S. Yamada, I. Yokoe: Tetrahedron Letters, No. 39, 4701 (1966).
*2 This paper also forms part VI of "Studies on N-Oxides of π-Deficient N-Heteroaromatics," for previous paper see ref. 3).
*3 All molecular formulae indicated in this paper were supported by acceptable elemental analyses. Melting points are uncorrected.

1) M. Ishikawa, S. Yamada, C. Kaneko: This Bulletin, **13**, 747 (1965); M. Ishikawa, S. Yamada, H. Hotta, C. Kaneko: *Ibid.*, **14**, 1102 (1966).
2) C. Kaneko, S. Yamada: *Ibid.*, **14**, 555 (1966).
3) *Idem*: Rept. Res. Inst. Dental Materials, Tokyo Medico-Dental University, **2** (9), 804 (1966). See also, C. Kaneko, S. Yamada, M. Ishikawa: Tetrahedron Letters, No. 19, 2145 (1966).
4) C. Kaneko, S. Yamada, I. Yokoe, N. Hata, Y. Ubukata: Tetrahedron Letters, No. 39, 4729 (1966).
5) J.K. Landquist, G.J. Stacey: J. Chem. Soc., **1953**, 2828.