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244. Shoji Shibata and Yukio Ogihara*1 : Metabolic Products of Fungi. XXIII.*2 On Ustilaginoidins. (3).*2 The Structures of Ustilaginoidins B and C.

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In the preceding report,[1,2] the structure of the main coloring matter of *Ustilaginoidea virens* (Cooke) Takahashi, ustilaginoidin A, has been elucidated as being represented by 2,2′-dimethyl-5,5′,6,6′8,8′-hexahydroxy-9,9′-bi[4*H*-naphtho[2,3-*b*]pyran-4-one] (I).

Two other coloring matters were separated from the mold and named ustilaginoidins B and C, respectively. The pigments, ustilaginoidins A, B and C, in the crude extracts, were obtained in a proportion of about 80:15:5.

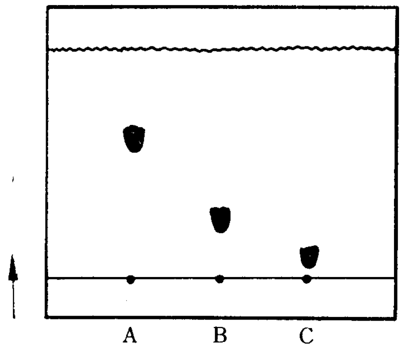


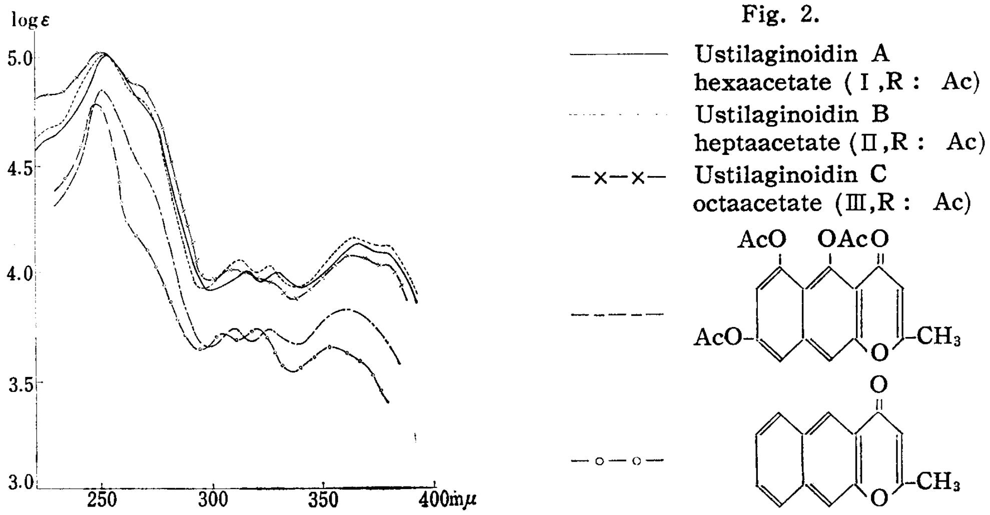
Fig. 1.

Solvent : Benzene-acetone (4:1)
Plate : "Silica-rider" treated with oxalic acid

All these pigments showed the similar appearance giving no melting point below 300°, but were separable by thin layer chromatgraphy (Fig. 1). According to Schmid and Seiler,[3] the naphthopyrones of linear and angular structures can be distinguished by the ultraviolet spectra. The ultraviolet spectral curves of ustilaginoidins A, B and C are superimposable each other, and those of peracetates are almost completely parallel with those of norrubrofusarin peracetate and 2-methyl-4*H*-naphtho[2,3-*b*]pyran-4-one[3] (Fig. 2). This suggests that ustilaginoidins A, B and C possess the same carbon skeleton and the chromophore system of norrubrofusarin, that is the linear type naphtho-pyrone system.

The analytical figures showed that the molecular formulas $C_{28}H_{18}O_{11}$ and $C_{28}H_{18}O_{12}$, are adopted for ustilaginoidins B and C, respectively. These results suggested that

Fig. 2.



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*2 Part XXII (2). : This Bulletin, **11**, 1179 (1963).

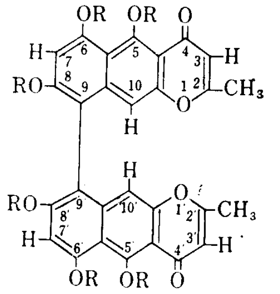
1) S. Shibata, A. Ohta, Y. Ogihara : *Ibid.*, **11**, 1174 (1963).

2) S. Shibata, Y. Ogihara A. Ohta : *Ibid.*, **11**, 1179 (1963).

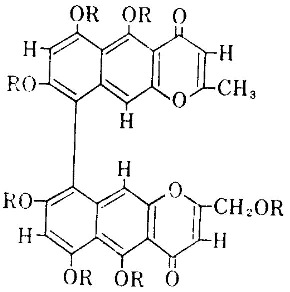
3) H. Schmid, H. Seiler : Helv. Chim. Acta, **35**, 1991 (1952).

ustilaginoidins B and C would be homologs of ustilaginoidin A (I : R=H) whose substituents at the 2 and 2′ positions are CH_3 and CH_2OH in the former (II : R=H), and both CH_2OH in the latter (III : R=H).

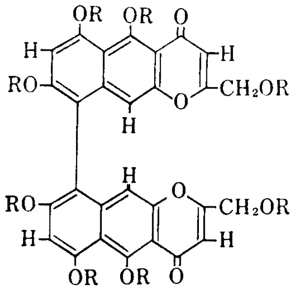
The nuclear magnetic resonance spectra of peracetates of ustilaginoidins A, B and C (I～III : R=Ac) were measured, and all the signals were assigned as indicated below to confirm the proposed structures. The signal of $\underline{CH_2}$ of carbinol acetate grouping in the 2 position of ustilaginoidin B appeared at τ : 5.11, whose magnitude was exactly half of that given by ustilaginoidin C (2 CH_2OAc at 2 and 2′ positions).



I



II



III

NMR Spectral Signals[a] (in $CDCl_3$)

$6O\underline{Ac}$	τ :	8.07, 7.51, 7.39
4H	τ :	2.82, 2.74
2H (at $C_{(3)(3')}$)	τ :	4.00
$2CH_3$	τ :	7.75
$6O\underline{Ac}$	τ :	8.06, 7.50, 7.38
$1CH_2O\underline{Ac}$	τ :	7.88
$1C\underline{H_2}OAc$	τ :	5.11
4H	τ :	2.71, 2.73, 2.77, 2.82
$\underline{H}$ (at $C_{(3)}$)	τ :	3.99
$\underline{H}$ (at $C_{(3')}$)	τ :	3.81
$\underline{CH_3}$	τ :	7.74
$6O\underline{Ac}$	τ :	8.06, 7.49, 7.38
$2CH_2O\underline{Ac}$	τ :	7.88
$2C\underline{H_2}OAc$	τ :	5.11
4H	τ :	2.78, 2.71
$\underline{H}$ (at $C_{(3)(3')}$)	τ :	3.81

[a] All the signals recorded above are singlets.

The chemical shifts observed at the signals of aromatic protons of ustilaginoidin B peracetate would be regarded to be caused by the unsymmetric effect of ring current.

Experimental

Isolation of Ustilaginoidins B and C——The crude pigment extracted from the smutted balls growing on the spikes of rice plant by the infection of *Ustilaginoidea virens* (Cooke) Takahashi was separated chromatographically over a silicic acid column to give 3 bands using benzene-Me_2CO (4:1) mixture as the developing solvent.

Ustilaginoidin A was obtained from the main bottom band, and ustilaginoidins B and C were isolated subsequently from the remaining two upper bands.

Ustilaginoidin B was recrystallized from dioxan to give dark red plates, m.p. >300°, $[\alpha]_D^{25}$ −360° (dioxan). *Anal.* Calcd. for $C_{28}H_{18}O_{11}\cdot(C_4H_8O_2)_2$: C, 61.20; H. 4.81. Found : C, 61.49; H, 4.65. *Anal.* Calcd. for $C_{28}H_{18}O_{11}$ (dried over 180° *in vacuo*) : C, 63.45; H, 3.45. Found : C, 63.17; H, 3.64.

Ustilaginoidin C was also recrystallized from dioxan to give dark red plates, m.p. >300°, $[\alpha]_D^{25}$ −260° (dioxan). *Anal.* Calcd. for $C_{28}H_{18}O_{12}$ (dried over 180° *in vacuo*) : C, 59.83; H, 4.71. Found : C, 59.55; H, 4.78. The other physical and chemical properties of ustilaginoidins B and C are almost same as described for ustilaginoidin A.[1]

Ustilaginoidin B Heptaacetate——On acetylation with Ac_2O and pyridine, ustilaginoidin B afforded heptaacetate, which was isolated from the second band of the silica gel chromatogram developed by a mixture of benzene and Me_2CO (4:1). Colorless powder (from EtOH), m.p. 170°. *Anal.* Calcd. for $C_{42}H_{32}O_{18}$: C, 61.17; H, 3.88. Found: C, 61.13; H, 4.00. UV λ_{max}^{EtOH} mμ (log ε) : 250 (5.02), 316 (4.06), 329 (4.03), 363 (4.17). IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 1770, 1745 (phenolic and alcoholic acetate C=O), 1660 (C=O), 1620 (aryl).

Ustilaginoidin C Octaacetate——Ustilaginoidin C was acetylated, and the product was treated as above described for ustilaginoidin B heptaacetate. Colorless powder (from EtOH), m.p. 140°. *Anal.* Calcd. for $C_{44}H_{34}O_{20}$: C, 59.86;H, 3.85. Found : C, 59.93; H, 3.98. UV λ_{max}^{EtOH} mμ (log ε) : 250 (5.03), 312 (4.02), 325 (3.97), 363 (4.09). IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1770, 1745 (phenolic and alcoholic acetate), 1660 (C=O), 1620 (aryl).

The NMR spectra were determined at 60 Mc. in $CDCl_3$ solution using Varian Associates A-60 type instrument.

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Summary

The structures of ustilaginoidin B, $C_{28}H_{18}O_{11}$, m.p. >300°, $[\alpha]_D^{25}$ −360° (dioxan) and ustilaginoidin C, $C_{28}H_{18}O_{12}$, m.p. >300$_o$, $[\alpha]_D^{25}$ −260° (dioxan) which were isolated as the pigments of *Ustilaginoidea virens* (Cooke) Takahashi, were studied mostly by the NMR spectral analyses of their peracetates to conclude as being formulated as II (R=H) and III (R=H), respectively.

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