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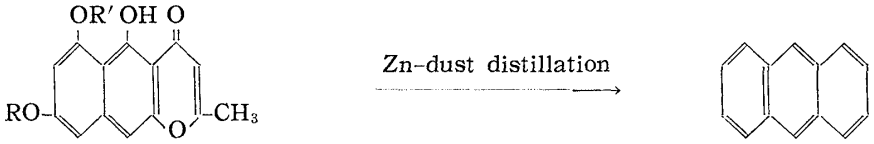
192. Shoji Shibata, Yukio Ogihara,*1 and Akihiro Ohta*2 : Metabolic Products of Fungi. XXII.*3 On Ustilaginoidins. (2).*3,*4 The Structure of Ustilaginoidin A.

(*Faculty of Pharmaceutical Sciences, University of Tokyo**1)

As described in the preceding paper,*3 the alkaline degradation of ustilaginoidin A, afforded acetone and an unstable polyhydroxy compound which was suggested spectroscopically as being 1-phenylnaphthalene or 1,1′-binaphthalene derivative. This result revealed that the skeleton of ustilaginoidin A would be 2-methyl-4*H*-naphthopyran-4-one whose analogs were found in nature as fungal pigments, rubrofusarin[1~4] (2-methyl-8-methoxy-5,6-dihydroxy-4*H*-naphtho[2,3-*b*]pyran-4-one) (I) of *Fusarium culmorum* (W.G. Smith) Sacc. and fonsecin[5] (2-methyl-6-methoxy-5,8-dihydroxy-4*H*-naphtho[2,3-*b*]pyran-4-one of *Aspergillus fonsecaeus* (ultraviolet mutant of N.R.R.L. 67).

The formation of anthracene by zinc dust distillation of ustilaginoidin A was also explicable by the conversion of 2-methyl-4*H*-naphthopyran-4-one structure.



I : R=CH_3, R′=H Rubrofusarin
II : R=R′=H Norrubrofusarin
III : R=H, R′=CH_3 Fonsecin

Ustilaginoidin A gave an ultraviolet spectral curve almost parallel with that given by nor-rubrofusarin (II) (Fig. 1).

The analytical figures and molecular weight of ustilaginoidin A suggested that it would be a dimer of nor-rubrofusarin,*5 and hence the alkaline degradation products

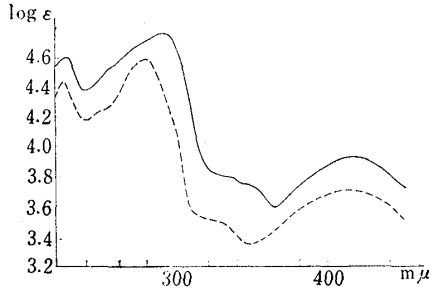


Fig. 1.
—— Ustilaginoidin
------ Nor-rubrofusarin

*1 Hongo, Tokyo (柴田承二, 荻原幸夫, 太田明広).
*2 Present address : Institute of Physical & Chemical Res., Kamifujimae, Bunkyo-ku, Tokyo.
*3 Part (1) : This Bulletin, **11**, 1174 (1963).
*4 A part of this work was presented before VIth Japanese Symposium on the Chemistry of Natural Products (Sapporo, July, 1962). Proceeding p. 47.
*5 A further evidence by the UV spectral analysis (cf. H. Schmid, H, Seiler : Helv. Chim. Acta, **35**, 1991 (1952)) excluding an angular type naphthopyrone structure of ustilaginoidin A will be discussed in the forthcoming report of this series.

1) J.N. Ashley, B.C. Hobbs, H. Raistrick : Biochem. J. (London), **31**, 385 (1937).
2) H. Tanaka, T. Tamura : Tetrahedron Letters, No. 4, 151 (1961); Agr. Biol. Chem., **27**, 48 (1963).
3) G.H. Stout, D.B. Dreyer, L.H. Jensen : Chem. & Ind. (Londn), 289 (1961).
4) G.H. Stout, L.H. Jensen : Acta Cryst, **15**, 451 (1962).
5) F. Stodola, *et al.* : Nature, **195**, 502 (1962).

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Table I. Infrared Spectral Absorption at 1770~1550 cm^{-1} Region

Compounds	$\nu_{C=O}$	Aromatic	Double bonds
Ustilaginoidin A (Ust. A)[a]	1645	1615	1585
Nor-rubrofusarin	1650	1610	1580
Ust. A tetraacetate	1769, 1645	1620	1590
Ust. A hexamethyl ether	1645	1605	1560
Product A octaacetate	1765, —	1623	1600
Product A octamethyl ether	—	1615	1595
Product B	1638	1600	1568
Product B dimethyl ether	1716	1616	1585
Rubrofusarin dimethyl ether	1655	1615	1565

a) Measured in KBr-tablet; unless otherwise stated, the spectra were measured in $CHCl_3$ solution.

A and B would be the corresponding binaphthalene derivatives. This presumption has been supported by the following infrared and nuclear magnetic resonance spectral analyses of ustilaginoidin A and its degradation products.

The C=O band shown in the infrared spectrum of ustilaginoidin A (1645 cm^{-1}) disapeared in that of product A.

The product B gave C=O band at 1638 cm^{-1}, which shifted to 1716 cm^{-1} on methylation of the hydroxyl group. Thus the ring cleavage of ustilaginoidin A hexamethyl ether by alkali resulted $-COCH_3$ and hydrogen bonded -OH in the product B.

This agreed the presence of 2-methylnaphthopyran-4-one ring system in ustilaginoidin A.

The nuclear magnetic resonance spectra of ustilaginoidin A hexamethyl ether, product B, product B dimethyl ether and product A octamethyl ether were measured.

Ustilaginoidin hexamethyl ether gave nuclear magnetic resonance signals (in $CHCl_3$) at τ=7.83 (singlet : CH_3 at the α,α'-position of γ-pyrone ring), τ=6.19, 5.94, 5.89 ($6CH_3O$ at the positions 5,5′, 6,6′, and 8,8′), τ=4.18 3.38, and 3.18 (singlets) which corresponded to the aromatic ring protons at the positions 3,3′, 7,7′, and 10,10′, respectively.

As a reference, the nuclear magnetic resonance spectrum of rubrofusarin dimethyl ether was measured (in $CHCl_3$), which gave a methyl signal at τ=7.71, methoxyl signals at τ=6.07 (duplicated) and 6.14, and the aromatic ring proton signals at τ=4.07 (singlet), 3.62 (doublet J=2.46 c.p.s.) and 3.45 (doublet J=2.46 c.p.s). One aromatic proton signal would be overlapped with the absorption of chloroform.

The singlet aromatic proton signal corresponded to pyrone ring proton at 3, and the doublets would be caused by the spin-spin coupling of *meta*-situated aromatic ring protons at 7 and 9.

The nuclear magnetic resonance spectrum of product B showed signals at τ=7.16 ($CO-C\underline{H}_3$), 6.22, 6.06, 5.90 ($OC\underline{H}_3$), 3.65, 3.32 (aromatic ring protons) and −1.78 (hydrogen bonded hydroxyl proton). On methylation of hydroxyl group of the product B, the signal at τ=−1.78 disappeared, the $COC\underline{H}_3$ signal shifted to τ= 7.47 and 4 equivalent signals appeared at τ=6.59, 6.23, 6.12, and 5.91 to represent $OC\underline{H}_3$ groupings. The aromatic ring protons of product B dimethyl ether gave the signals (singlets) at τ=3.80 and 3.32.

The permethyl ether of product A showed 4 methoxyl signals at τ=6.53, 6.23, 6.03, and 5.91 and the signals of aromatic ring protons at τ=3.94 (doublet J=2.45 c.p.s.), 3.64 (doublet J=2.45 c.p.s.) and 3.31 (singlet). The doublet signal of aromatic protons would be resulted by the *meta* spin-spin coupling. All these evidences are compatible with above mentioned presumption for the structure of ustilaginoidin A.

The *meta* coupling of aromatic protons which was given by rubrofusarin dimethyl ether was not observed in the nuclear magnetic resonance spectrum of ustilaginoidin

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hexamethyl ether. This fact excluded the case of linking two nor-rubrofusarin moieties at 10 and 10′, and indicated the possibility of bonding at 9 and 9′ or 7 and 7′ positions.

The optical activities observed in ustilaginoidin A, its acetate and methyl ether, as well as, their alkaline degradation products A and B, would be resulted by the restricted rotation about single bond linkage.

Such a stable optical asymmetry has been shown by some synthetic α,α'-binaphthyl[7] and α,α'-bianthranyl derivatives,[8] whereas 2,2′,6,6′-tetramethoxybiphenyl or β,β'-binaphthyl derivatives are readily racemised.

This suggested that the norrubrofusarin moieties of ustilaginoidin A would be connected at α and α' or 9 and 9′-positions.

A higher shift of the proton signal ($\tau=3.18$) at $C_{(10,10')}$ of ustilaginoidin A hexamethyl ether was observed in comparison with that given by the proton at the corresponding position in norrubrofusarin trimethyl ether.

It would be resulted by the effect of ring current of the interlinking naphthopyrone moieties in the former.

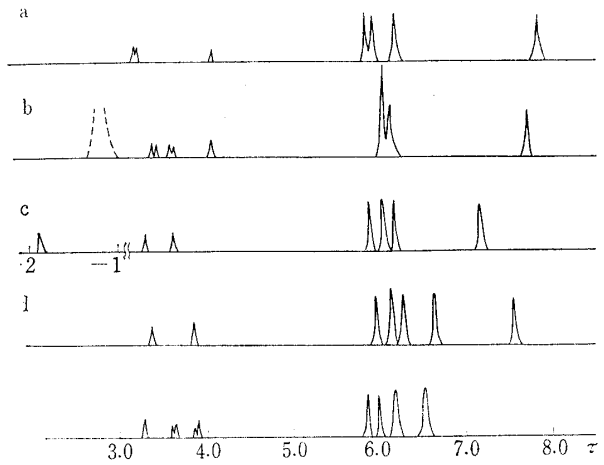

Fig. 2.
a : Ustilaginoidin A hexamethyl ether
b : Rubrofusarin dimethyl ether
c : Product B
d : Product B dimethyl ether
e : Product A octamethyl ether

Two naphthopyrone or naphthalene moieties are completely equivalent in the nuclear magnetic resonance spectra of ustilaginoidin A and its alkaline degradation products, giving no chemical shifts at the individual signal.

According to all the chemical and physical evidences provided in the preceding and present papers, ustilaginoidin A can be formulated as IV, by which all the degradation reactions are reasonably elucidated.

Ustilaginoidin A is unique among the naturally occurring optical active compounds, as its optical activity is only resulted from the molecular asymmetry by the restricted rotation of C-C linkage.

The nuclear magnetic resonance spectra were measured in dil. $CHCl_3$ and $CDCl_3$ solutions (ca. 20~30 mg. of samples in 0.5 ml. of the solvent) using Varian Associates DP. 60 and A-60 NMR Spectrometer operating at 60 Mc.p.s.

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7) W.M. Stauley, R. Smith : Rec. trav. chim. **48**, 1035 (1929).
8) F. Bell, D.H. Waring : J. Chem. Soc., **1949**, 1579.

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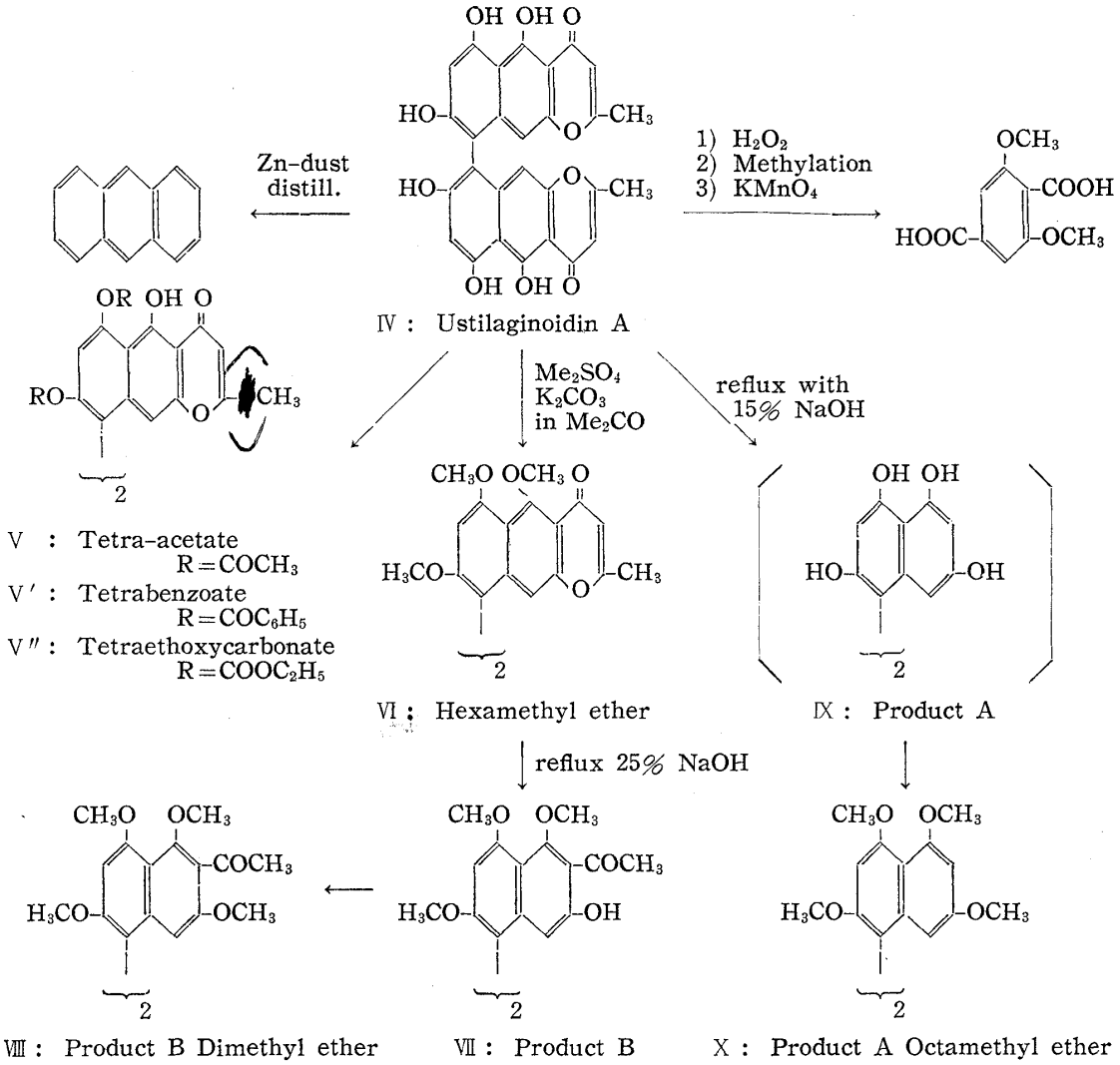

Summary

Ustilaginoidin A has been formulated as 2,2′-dimethyl-5,5′,6,6′,8,8′-hexahydroxy-9,9′-bis(4*H*-naphtho[2,3-*b*]pyran-4-one) on the basis of the infrared and nuclear magnetic resonance spectral analyses of ustilaginoidin A and its degradation products, product A and product B and their derivatives.

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