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THE ABSOLUTE CONFIGURATIONS OF USTILAGINOIDINS

S. Shibata and Y. Ogihara
Faculty of Pharmaceutical Sciences, University of Tokyo

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USTILAGINOIDIN, a red colouring matter obtained from the smutted balls formed by the infection of Ustilaginoidea virens (COOKE) TAKAHASHI on the spikes of rice plant, was first studied by Yabuta and Sumiki[1], and it has recently been found by us that the pigment is accompanied by two other homologous compounds[2] which are separated by silicic acid column chromatography. We propose to name these pigments as ustilaginoidins A, B, and C.

The structure of ustilaginoidin A, $C_{28}H_{18}O_{10}$, m.p. > 300°, $[\alpha]_D$ -384° (dioxane) was established as being 2.2'-dimethyl-5,5',6,6',8,8'-hexahydroxy-9,9'-bi[4H-naphtho[2,3-b]pyran-4-one] (Ia)[3], and ustilaginoidin B, $C_{28}H_{18}O_{11}$ and C, $C_{28}H_{18}O_{12}$, were reasonably elucidated by the structures (Ib) and (Ic), respectively[4].

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[2] S. Shibata, A. Ohta and Y. Ogihara, Chem. Pharm. Bull., 11 (1963) in press.

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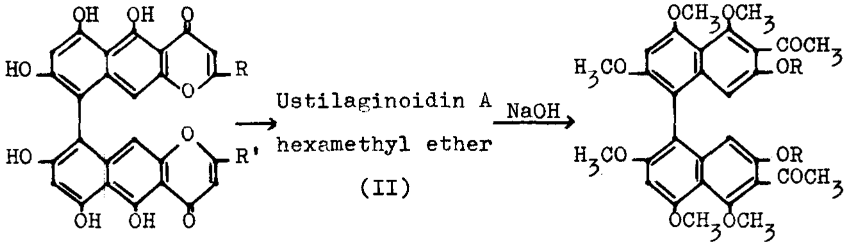

(Ia) R=R'=CH_3
(Ib) R=CH_3 R'=CH_2OH
(Ic) R=R'=CH_2OH

(III) R=H
(IV) R=CH_3

These pigments are unique among the natural products because of their optical activities caused only by the intramolecular restricted rotation of the C-C linkage without presence of any asymmetric carbon atom in the molecules.

The absolute configurations of 1,1'-biphenyls, 1,1'-binaphthyls[5] and 1,1'-bianthryls[6] were investigated recently using optical rotatory dispersion. A positive long wavelength Cotton effect indicated the R-configuration and a negative effect the S-configuration.

Therefore, the optical rotatory dispersions have been measured to determine the absolute configurations of ustilaginoidins.

The positive Cotton effects at the higher wave length region were shown by ustilaginoidin A, its hexamethyl ether, and the peracetates of ustilaginoidins A, B and C to indicate their R-configurations.

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[6] G.M. Badger, R.J. Drewer, and G.E. Lewis, J. Chem. Soc., 4268 (1962).

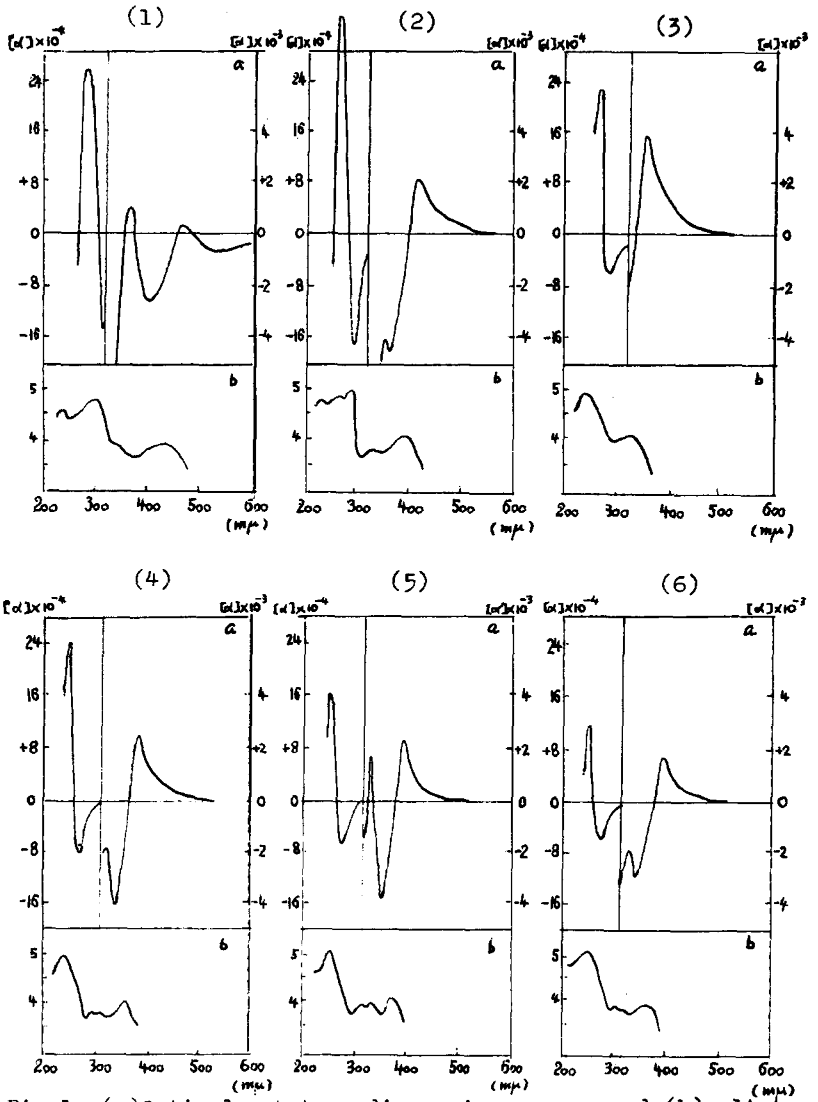

Fig.1. (a)Optical rotatory dispersion curves and (b) ultraviolet absorption curves of (1) ustilaginoidin A,(2)ustilaginoidin A hexamethyl ether,(3) 1,1',3,3',6,6',8,8'-octamethoxy-2,2'-diacetyl-5,5'-binaphthalene,(4)(5)(6) peracetates of ustilaginoidins A,B, and C,**respectively**, in dioxane.

1.1',3,3',6,6',8,8'-Octamethoxy-2.2'-diacetyl-5.5'-binaphthalene (IV) which was derived from ustilaginoidin A hexamethyl ether by alkaline degradation followed by methylation also showed to possess R-configuration by the optical rotatory dispersion.

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