

Detailed investigation on the biological activities of the peptide Bo-III are now in progress. As we have mentioned,⁸⁾ occurrence of this peptide Bo-III in *Bombina orientalis* also suggests the presence of different kininogens in animal kingdom.

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Mode of Morphological Forms of Crystalline Inorganic Component in Plants: Silicon Bodies in Wheat

I have been carrying out a series of studies on low-temperature ashed image¹⁻⁶⁾ of biological tissues, especially of plant tissues, obtained by "Low-temperature Plasma Ashing Method for Biological Materials" originated with me. Phytological studies on ashed image are especially important in observation the crystalline inorganic components, such as silicon bodies, calcium oxalate crystals, and cystoliths. My previous studies have revealed the characteristic shape, size, arrangement, and distribution of these crystalline inorganic components in various plants. In addition, my recent experiments provided numerous phenomena which suggested the presence of a regulatory mechanism in the morphological behavior of these crystalline inorganic compounds.

Crystalline inorganic components in plants have not been taken up as an attractive academic subject, other than that they are one of waste products of plants, because such components themselves do not show any physiologically interesting activity. In addition, the technique and method for observing these crystalline inorganic components are attended with unavoidable chemical and technical limitations, difficulty, and defects this study has not made much

- 1) K. Umemoto and K. Hozumi, *Chem. Pharm. Bull.* (Tokyo), **19**, 217 (1971).
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- 4) K. Umemoto and K. Hozumi, *Mikrochim. Acta*, **1972**, 748; *idem, Microchem. J.*, **17**, 689 (1972).
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progress. Consequently, no examinations have yet been made on these crystalline inorganic components from genetic aspects, and nothing is known about the behavior of such components.

In order to clarify the mode of these crystalline inorganic components from their low-temperature ashed image obtained by oxygen plasma treatment, I resolved to examine the presence of any genetic tendency in their morphological form and, as the first step, I took up the silicon bodies with the chemical composition of SiO_2 ⁷⁾ as one of the crystalline inorganic components. As the experimental material, the flag leaves of wheat which contains a large amount of silicon bodies and which is phylogenetically authorized were used; *Triticum aegilopoides* BAL. (genome AA, 101-1⁷⁾) of an one-grained wheat, *Aegilops speltoides* TAUSCH (genome SS, 2-1⁷⁾) and its amphidiploid (genome SSAA, T411-1⁷⁾), another one-grained wheat, *T. monococcum* L. (genome AA, 104-1⁷⁾) and a Timopheevi wheat, *T. timopheevi* (genome AAGG, 107-1⁷⁾) and its amphidiploid (genome AAGGAA, 1822A-1⁷⁾).

Results of experiments revealed the following facts;

A) Amphidiploid between *T. aegilopoides* and *A. speltoides*

(1) Silicon bodies are arranged longitudinally on the leaf vein and along it in parallel, approximately in fastner type (Fig. 1-A). The same arrangement is not seen in *A. speltoides* and is observed characteristically in *T. aegilopoides* (Fig. 1-B).

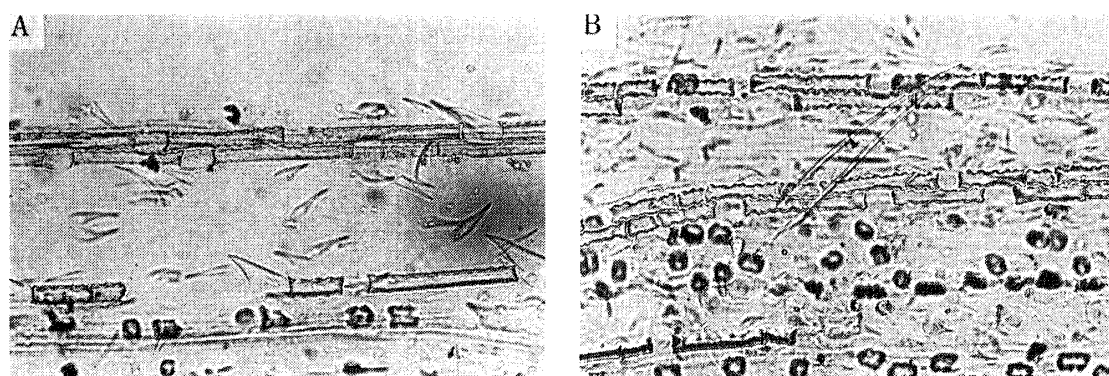


Fig. 1. Low-temperature Ashed Image of the Flag Leaves of Wheat

A: Amphidiploid between *T. aegilopoides* and *A. speltoides*, $\times 100$
 B: *T. aegilopoides*, $\times 100$

(2) Long and thin silicon bodies are arranged linearly along and in parallel with the vein. These crystals have double the length of the longest silicon bodies present in *T. aegilopoides* and have less irregular profiles. This is characteristically found in *A. speltoides*.

B) Amphidiploid between *T. monococcum* and *T. timopheevi*

(1) Triangular silicon bodies with specific shape are sometimes seen on the vein. The same shape is present only in *T. timopheevi* and not in *T. monococcum*.

(2) Although the number is small and linear linking is short, silicon bodies arranged in a fastner type are observed. This is a characteristic arrangement observed in *T. monococcum* but not in *T. timopheevi*.

(3) Quadrilateral silicon bodies with undulate profiles are arranged on the vein, the grade of the undulation being intermediate of those of *T. monococcum* and *T. timopheevi*.

C) The behavior of morphological forms of silicon bodies in these wheat leaves agrees well with the genetic mode of the samples such as form of the ear and other outer morphological forms of the wheat.

It is still obscure at present what, if any, genetic rule controls the morphological form of silicon bodies as one of crystalline inorganic components in wheat. However, it has become

7) Sample number of phylogenetically preserved species, Plant Germ-Plasm Institute, Faculty of Agriculture, Kyoto University.

clear from the present series of experiments that the morphological form of silicon bodies in the wheat species examined is undeniably inherited by their descendants.

It is interesting that *T. aegilopoides* (wild type) and *T. monococcum* (cultivated type), homogenetic AA from genome analysis, have some items common to both and specific to samples having AA genome such as the shape, size, and arrangement of silicon bodies, and some items that are considerably different in the two species.

Further details along these experiment are still in progress. Similar experiments are also being carried out on other crystalline inorganic components and some interesting results are being obtained which will be reported at a later date.

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A Stereoselective Synthesis of 16 β -Substituted-17-oxosteroids

During hormonal studies on synthetic steroids, 17 β -hydroxy-16 β -substituted-estr-4-en-3-ones (**1**) were found to have a strong antiandrogenic activity.¹⁾ This is to report a facile introduction of β -substituents at position 16 of steroids by a kinetically controlled reaction.

Treatment²⁾ of **2a, b, c**, prepared from 16-oxosteroid by Grignard reactions, with H₂SO₄ in methanol for several minutes at 25° gave **3a**,³⁾ mp 94° (81%), **3b**, mp 137° (61%), and **3c**, mp 151° (85%), each as a single product. The stereochemistry at position 16 was investigated mainly by examining 16, 17 proton-proton coupling constants of the following compounds. NaBH₄ reduction of **3a, b, c** gave **4a**, mp 97°, 17H: δ 3.68 ($J=9$ Hz),⁴⁾ **4b**, mp 140°, δ 3.74 ($J=9$ Hz), and **4c**, mp 176°, δ 3.92 ($J=11$ Hz), respectively. Treatment of **4b** with *p*-toluenesulphonic acid gave a cyclic compound (**5**), mp 152°, δ 4.01 ($J=10$ Hz). The formation of **5** and its coupling constant suggests that 17-OH takes *cis* position relative to 16-R in **4a, b, c**.

On the other hand, reaction of the 17 β -acetate (**6**) with POCl₃ in dry pyridine yielded **7**, mp 148°, which was hydrogenated (PtO₂, EtOH) to give, after separation on silica gel, a 16-ethyl derivative (**8**), mp 134° and the isomer (**9**), mp 114° in a ratio of 1:1. Hydrolysis of them afforded 16-ethyl-17 β -hydroxy compounds (**4a**) and (**10**),⁵⁾ mp 74°, δ 3.23 ($J=6$ Hz). Since 17-OH and 16-R of **4** are in *cis*-configuration, 16-ethyl of **4a** and its isomer (**10**) should take β - and α -orientation, respectively. We have further data to support that the coupling constants of 16 α H-17 α H and 16 β H-17 α H are around 9 Hz and 6 Hz, respectively.

1) The details of the syntheses and biological activities of **1** will be reported elsewhere.

2) Reaction conditions are critical. Prolongation of the reaction gives rise to the 16-epimeric mixtures.

3) J. Hooz, M. Gunn and H. Kono, *Can. J. Chem.*, **49**, 2371 (1971).

4) NMR spectra were measured at 100 MHz with Me₄Si as the internal standard using CDCl₃ as a solvent.

5) N.V. Organon, Belg. Patent 660312.