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 item 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 16β-Substituted-17-oxosteroids

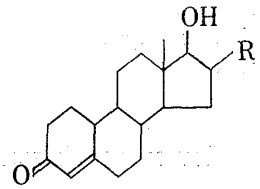
During hormonal studies on synthetic steroids, 17β-hydroxy-16β-substituted-estr-4-en-3-ones (**1**) were found to have a strong antiandrogenic activity.[1] This is to report a facile introduction of β-substituents at position 16 of steroids by a kinetically controlled reaction.

Treatment[2] of **2a, b, c**, prepared from 16-oxosteroid by Grignard reactions, with H_2SO_4 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. $NaBH_4$ 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.**

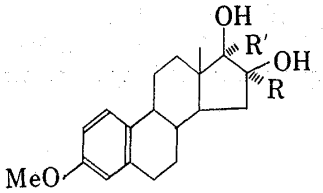
On the other hand, reaction of the 17β-acetate (**6**) with $POCl_3$ in dry pyridine yielded **7**, mp 148°, which was hydrogenated (PtO_2, EtOH) to give, after separation on silica gel, a 16-ethyl derivative (**8**), mp 134° and the isomer (**9**), mp 114° in a ratio of 1:1. Hydrolysis of them afforded 16-ethyl-17β-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 16αH-17αH and 16βH-17αH 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 Me_4Si as the internal standard using $CDCl_3$ as a solvent.
5) N.V. Organon, Belg. Patent 660312.

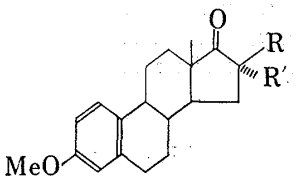
For clarification of the dehydration mechanism, we performed the following experiments: **2c** was oxidized (pyridine-SO_3, DMSO)[6] and reduced ($NaBD_4$, MeOH) to give **2d**, mass *m/e* 379 (M^+). This was treated with H_2SO_4 in methanol, whereby no deuterio-compounds but **3c** were obtained. On the other hand, when **3d**, mass *m/e* 361 (M^+), prepared by deuteration of **3c** with D_2SO_4 in CD_3OD, was subjected to the same reaction condition, the loss of deuterium[7] during the reaction was less than 20%. These results indicate that the reaction proceeds with vinyldehydration[8] and kinetically controlled ketonization.[9] On the ketonization step, proton favors to attack less hindered α-side[10] of the postulated intermediate (**11**) to give **3a, b, c.**

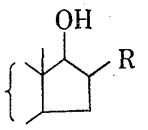


1 : R=alkyl

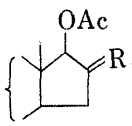


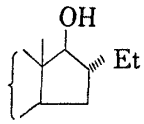
2a : R=Et ,R′=H **3a**
2b : R=$CH_2CH=CH_2$,R′=H **3b**
2c : R=C_6H_5 ,R′=H **3c**
2d : R=C_6H_5 ,R′=D **3d**





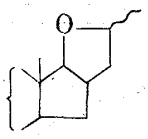
4a : R=Et
4b : R=$CH_2CH=CH_2$
4c : R=C_6H_5



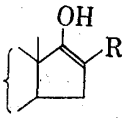


10

6 : R=
7 : R= =CHMe
8 : R=
9 : R=



5



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