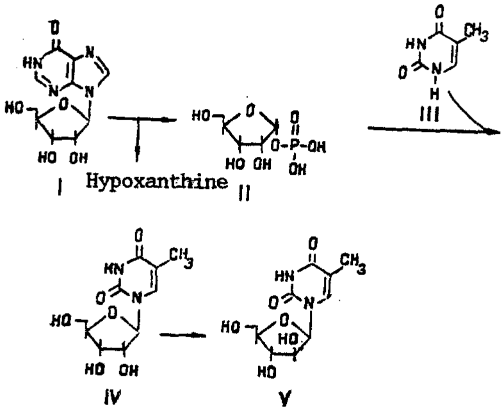

1-(β-D-Arabinofuranosyl)thymine (V): mp 246-247°C; Rf 0.73 ($CHCl_3$–MeOH (4:1); Silufol UV-254 plates). UV spectrum: $\lambda_{max}^{H_2O}$, pH 7, nm: 268 (log ε 10.3). PMR (100 MHz, DMSO): 7.5 (1H, s, H-6), 5.94 (1H, d, H-1', $J_{1',2'}$ = 4 Hz), 3.96 (2H, m, H-2', 3'), 3.63 (3H, m, H-4', 5', 5"), 1.77 (3H, s, CH_3).

Found, %: C 46.40; H 5.35; N 10.65. $C_{10}H_{14}N_2O_6$. Calculated, %: C 46.51; H 5.46; N 10.84 M 258.2.

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INFLUENCE OF THE FREE CARBOXY GROUP OF GIBBERELLIN A_3 ON THE RATE OF ITS ISOMERIZATION IN AQUEOUS AMMONIA

A. G. Druganov and N. A. Pankrushina

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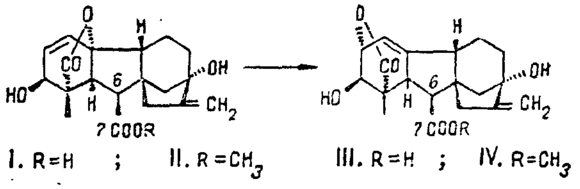
It is known that in aqueous alkaline solutions the phytohormone gibberellin A_3 (I) [1] and its methyl ester (II) are quantitatively converted into iso-A_3 (III) and the methyl ester of iso-A_3 (IV), respectively [2]. MacMillan et al. [3], investigating the mechanism of this reaction, assumed that the completeness of the ionization of the remote 7-carboxy group does not affect the occurrence of isomerization.



We have made a comparative study of the isomerization of compounds (I) and (II) in 1 M aqueous ammonia at 18°C with the initial concentrations of 0.04 M for (I) and 0.009 M for (II). The disappearance of substances (I) and (II) was monitored by the HPLC method on a reversed-phase column with detection at a wavelength of 200 nm [4]. For the methyl ester of

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Novosibirsk Institute of Organic Chemistry, Siberian Branch USSR Academy of Sciences. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 588-589, July-August, 1989. Original article submitted December 13, 1988.

A_3 (II) the period of half-conversion was 1 h, while for A_3 itself (I) it was 6 h 40 min, which corresponds to a retardation of the isomerization of (I) as compared with (II) by a factor of 6.7.

We explain the fact that gibberellin A_3 (I) with a free 7-carboxy group is converted into the isomerized product considerably more slowly than its methyl ester (II) by the influence of the 7-carboxylate anion. As suggested by MacMillan et al. [3], the process of allyl rearrangement takes place through the intermediate formation of an anion, and the propinquity of a 7-carboxylate anion will have a retarding influence on this reaction, as we have show experimentally.

The effect that has been detected of an accelerated alkaline isomerization of the methyl ester of A_3 (II) must be taken into account when working with mixtures containing this gibberellin, since the methylation of the mixtures isolated is a common procedure. This probably applies also to the esters of the related gibberellins A_7 and A_{32}.

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