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Conversion of β-Hydroxyethylhydrazine to Ethylene

ETHYLENE is known to be effective in inducing flowering in pineapple[1]. Compounds with similar activity include β-hydroxyethylhydrazine (BOH)[2], which has been suggested to induce flowering by reducing the auxin concentration in the plant[3], and which has been observed to inhibit the oxidation of tryptamine to indoleacetaldehyde by extracts of pea seedling[4]. But this theory was disputed, and it was suggested that BOH produces ethylene spontaneously, which then causes flowering and fruit abscission[5].

We have evidence that BOH is not converted directly to ethylene. After neat BOH had been degassed at ambient temperature and 0.1 mm pressure for 24 h, no ethylene was detected in the trap (−196° C) using mass spectrometry, which does not agree with the report[5] of a 1.4% conversion of BOH to ethylene in the same period. Furthermore, a dilute (4%) aqueous solution of BOH had evolved no gas after 7 days.

It has been suggested that formaldehyde and other carbonyl compounds catalyse the conversion of BOH to ethylene by the scheme shown in Fig. 1[5]. Therefore we added an equimolar amount of formalin solution to the aqueous BOH solution, but again no gas was evolved.

To establish the validity of the individual steps in Fig. 1, we attempted to prepare hydrazones of BOH. It has been reported that substituted β-hydroxyethylhydrazines react with carbonyl compounds to give derivatives of III*a* (tetrahydro-2H-1,3,4,-oxadiazine)[6–8]. In some cases[7,8], there is a rapid, temperature-dependent tautomerism between the tetrahydrooxadiazine and the hydrazone (that is, step II).

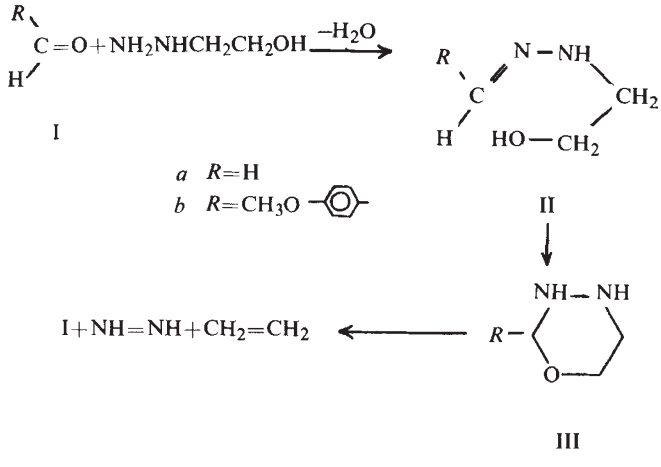

Fig. 1 Scheme for conversion of BOH to ethylene[5].

First we prepared the condensation product of BOH and *p*-anisaldehyde (I*b*) by refluxing equimolar amounts of these two compounds in benzene for 24 h, using a Dean–Stark apparatus. This yielded 52% of a pale yellow product, melting point 155–157° C, the infrared spectrum of which showed no C=N or O—H groups, but did show secondary N—H. We concluded that in this case the product was III*b*, the cyclized form. The remainder of the weight was accounted for by starting material, so that again there was no ethylene formation, even at the elevated temperature of the reaction.

We made two attempts to synthesize the unsubstituted tetrahydrooxadiazine III*a* from formaldehyde and BOH. The Dean–Stark method[7], and an aqueous reaction medium at ambient temperature[6], yielded nothing but starting materials, and no gas was seen to evolve. It is possible in this case that the equilibrium for formation of II*a* is very unfavourable. Clearly formaldehyde does not catalyse the formation of ethylene.

The ethylene purported to have originated from BOH[5] may have come from an entirely different source. Autoclaved rubber injection caps, used frequently in biological work, give off significant amounts of ethylene, even after 24 h[9]. Such caps were reported to have been used in the experiments in question[5], but they were not used by us. Because the caps give off ethylene continuously for a long period, they are a probable source of the gas.

We have found, therefore, that BOH does not in and of itself produce ethylene, and must therefore induce flowering in plants by some other means, perhaps by producing ethylene *in vivo* or reducing auxin concentration.

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