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PLANT GROWTH PROMOTING METABOLITES OF SCLEROTINIA SCLEROTIORUM

(II) THE SYNTHESIS OF SCLEROTININ B

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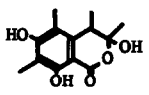
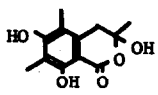
In our screening program to search new plant growth substances among fungus metabolites, we have found that the cultured filtrate of Sclerotinia sclerotiorum stimulated growth of rice seedling. The active principles, sclerotinin A and B in addition to sclerin (1), were isolated, and the structures of which were determined to have the structures I and II respectively on the basis of the spectroscopic and chemical evidences (2). Here we wish to report the synthesis of sclerotinin B, which supported the assigned structure completely.

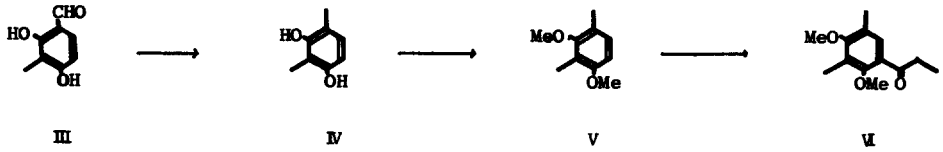
2-Methyl-4-formylresorcinol (III) was prepared from 2-methylresorcinol according to the method of W. Baker et al (3). Hydrogenation of III in acetic acid with palladium oxide at room temperature afforded 2,4-dimethylresorcinol (IV)(80%), mp 108°C (lit. mp 108-9°C) (3). Methylation of IV with methyl iodide and potassium carbonate in methyl ethyl ketone yielded a 2,4-dimethylresorcinol dimethyl ether (V)(82%), bp 84-5°C (3 mmHg). V was acylated with propionyl chloride and aluminium chloride in carbon disulfide at -5~-10°C to give a propiophenone (VI) (80%), bp 155-8°C (12 mmHg)(λ_{max}^{MeOH} mμ(log ε): 258(3.91), 300(infl. 3.22); $\nu_{C=O}^{CHCl_3}$ cm^{-1}: 1675) (4). VI was condensed with paraformaldehyde and dimethylamine hydrochloride in ethanol to give the Mannich base, which was, without purification, pyrolyzed at 160-70°C to yield a α-methylacrylophenone (VII) (70%), bp 122-4°C (4 mmHg)(λ_{max}^{MeOH} mμ(log ε): 266(3.54); $\nu_{C=O}^{CHCl_3}$ cm^{-1}: 1650). When VII was treated with conc. sulfuric acid at room temperature, 2-methylindanone (VIII) (80%), bp 145-8°C (3 mmHg)(λ_{max}^{MeOH} mμ(log ε): 266(4.15), 304(3.45); $\nu_{C=O}^{CHCl_3}$ cm^{-1}: 1688) was produced. The structure of VIII was confirmed by the IR and NMR spectra ($\delta_{TMS}^{CDCl_3}$: 3.93(3H, s, OCH_3), 3.77(3H, s, OCH_3), 3.24(1H, m, -CH-), 2.8~2.3(2H, m, $-CH_2-$), 2.20(6H, s, $=C-CH_3$), 1.29(3H, d, J=7.5 cps, $-CH-CH_3$). Oxidation of VIII with hydrogen peroxide and Treibs reagent in aqueous methanol at 80°C afforded a lactol (IX)(60%), mp 85-7°C (ν_{max}^{KBr} cm^{-1}: 3360(OH), 1683(O-C=O), which was identical with dimethylated product



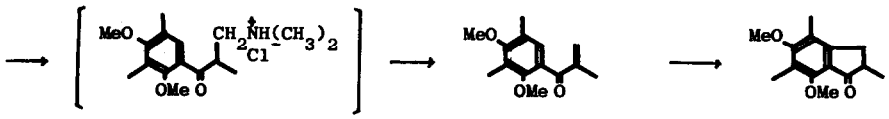
I



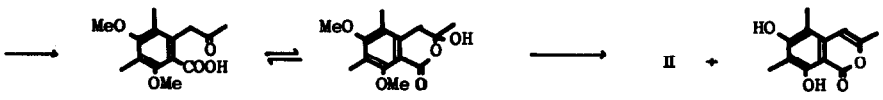
II



III IV V VI



VII VIII



IX' IX X

of natural sclerotinin B (II) in the IR spectra (in chloroform solution, $\nu_{C=O}^{CHCl_3}$ cm^{-1}: 1725 (broad). It was revealed by the spectroscopic evidences that IX presented in equilibrium with the keto-carboxylic acid (IX') in solution. IX (80 mg) was demethylated with boron tribromide in dichloromethane to give phenolic compounds. Chromatography of the mixture on silica gel column gave two products, one having mp 190-2°C (decomp.)(5 mg) and the other mp 207-8°C (20 mg). The former was identical with natural sclerotinin B (II) in the UV (in methanol and in alkaline methanol) and IR (in potassium bromide disk) spectra and on TLC plates. The latter (X) was identical with anhydrosclerotinin B, which was obtained from II by dehydrating with p-toluenesulfonic acid in benzene, in the mixed mp, UV (in methanol) and IR (in potassium bromide disk) spectra.

I and II promoted the growth of rice seedling at the concentration of 5 ppm in the rice seedling test performed in glass tubes (5). Moreover we have much interests in the series

of compounds derived from I and II as plant growth substances since they have the constitution analogous to sclerin which was revealed to have the plant growth promoting effect for various plants by Y. Satomura et al (1).

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