Biochemical Studies on "Bakanae" Fungus. Part 68.
Synthesis of Substances related to Gibberellins

Part XI* Synthesis of (±)-1,7-Dimethyl-6-ketogibba-A,4b-tetraene, a Degradation Product of Gibberellic Acid

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Epigibberic acid (I) afforded a ketone, C_{17}H_{18}O, of unknown structure when pyrolyzed on charcoal at 250°C. Recently the same ketone was obtained from gibberone (II) by treatment with sulfuric acid and structure (III) was suggested for it by considering both the spectral evidences and the mechanism of formation\(^2\).

An unambiguous synthesis of (±)-1,7-dimethyl-6-ketogibba-A,4b-tetraene\(^3\) (III) has now established the structure of the ketone. (±)-6-Ketogibberone (IV)\(^4\) in chloroform was treated with ethanedithiol and boron trifluoride etherate to afford the corresponding 8-dithioethyleneketal (V), m.p. 192~193°C. The thioketal (V) was boiled with deactivated Raney nickel in dioxane. After chromatographic purification of the product, the desired ketone (III), m.p. 114~115°C, was obtained. Its infrared (in chloroform) and ultraviolet (in ethanol) spectra were identical with those of the natural product kindly provided by Dr. J. MacMillan, Imperial Chemical Industries, Akers Research Laboratories, England.

**EXPERIMENTAL**

All melting points are not corrected.

(±)-6-Ketogibberone-8-dithioethyleneketal (V). To a solution of (±)-6-ketogibberone (IV, 1.9 g) in chloroform (30 ml) were added ethanedithiol (2 ml) and boron trifluoride etherate (2 ml). After having been left to stand for 12 hrs. at room temperature, the red-brown solution was poured into ice-water. The organic layer was washed with sodium bicarbonate solution, followed by sodium chloride solution
and dried over sodium sulfate. The residue, after removal of the solvent, was triturated with ether to afford 1.4 g (48%) of the thioketal. Leaflets from ethyl acetate-petroleum ether, m.p. 192–193°C. Anal. Found: C, 68.70; H, 6.05; S, 19.46. Calcd. for C_{19}H_{20}O_{2}S: C, 68.25; H, 6.14; S, 19.52%.

(−)-1,7-Dimethyl-6-ketogibba-A, 4b-tetraene (III).
The thioketal (V, 1.0 g) in dioxane (50 ml) and acetone (10 ml) was refluxed with Raney nickel W-7 (8 g, deactivated by treatment with boiling acetone for an hour) for 14 hrs. The catalyst was filtered off and the solvent removed in vacuo. Trituration with methanol gave the starting material (300 mg). The mother liquor gradually deposited a crystalline mass of the crude product (III, 220 mg). It was recrystallized twice from methanol but still contaminated with impurities. The impure ketone (50 mg) in ethyl acetate (0.5 ml) was chromatographed on alumina (8×1 cm) in n-hexane. Elution with n-hexane (30 ml) afforded the pure ketone (30 mg). Needles from methanol, m.p. 114–115°C. Anal. Found: C, 85.34; H, 7.79. Calcd. for C_{17}H_{18}O: C, 85.67; H, 7.61%. ν_{max} (Nujol) 1656, 1634, 1600, 1150, 792. λ_{max} (EtOH) m_{μ} (log ε) 232 (3.93), 238 (3.98), 295 (4.24), ∼324 (4.18).

2,4-Dinitrophenylhydrazone. Red needles from ethyl acetate, m.p. 259–261°C (dec.). Anal. Found: C, 66.02; H, 4.37; N, 13.55. Calcd. for C_{23}H_{22}O_{4}N_{4}: C, 66.01; H, 5.50; N, 13.39%. ν_{max} (Nujol) cm^{-1} 3300, 1614, 1596, 1330, 778. λ_{max} (CHCl_{3}) m_{μ} (log ε) 269 (4.26), 325 (3.97), 335 (3.97), 329 (4.07), 407 (4.55). cf. natural product1: λ_{max} (CHCl_{3}) m_{μ} (log ε) 269 (4.25), 325 (3.96), 410 (4.56).