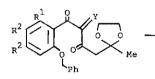
Total Synthesis of Fulvic Acid

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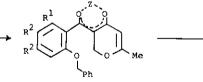
Synthesis of fulvic acid (9) was accomplished by a route involving a selective ozonization of (5a), obtained by a regioselective cyclization of (1a).

As a preliminary experiment, (5b), the basic skeleton in (9) was synthesized as follows. Treatment of (lb) with acidic condition (dil.HCl/THF or dil.H₂SO₄/ HOAc/THF) afforded a single cyclization product (2b). Application of Fujita's debenzylation method (Me_2S/BF_3 ·OEt₂) to the BF₂-complex (3b) of the pyrone (2b) followed by acidic cyclization (conc.HC1/HOAc) led to (5b).

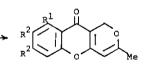
In the same manner, (la) was converted into the propenyl derivative (5a), whose selective ozonization in the presence of a dye (Oil Violet) as a internal indicator followed by the reduction with methylsulfide produced the aldehyde (6). Selective demethylation of (7), derived from (6), was carried out by treatment with AlCl₃-Me₂S to give (8). Finally conversion of (8) into (9) was acieved by the hydration (5% HCl/Me₂CO, 55°C, 24 h.).



la R¹=CH=CHMe, R²=OMe Y=H,CH₂S(O)Me



2a R¹=CH=CHMe, R²=OMe, Z=H $2b R^{1}=R^{2}=H, Z=H$ 1b $R^1 = R^2 = H$, $Y = CH_2$ or $H, CH_2S(0)Me$ 3a $R^1 = CH = CHMe$, $R^2 = OMe$, $Z = BF_2$ 3b $R^1 = R^2 = H$, $Z = BF_2$



4a R^1 =CH=CHMe, R^2 =OMe 4b $R^1 = R^2 = H$

