Total Synthesis of Fulvic Acid

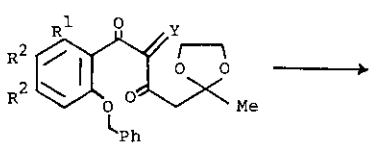
Sadamu Katayama, Toshiharu Todoroki, Masashige Yamauchi, and Toshio Watanabe

Faculty of Pharmaceutical Sciences, Josai University, Keyakidai, Sakado, Saitama 350-02, Japan

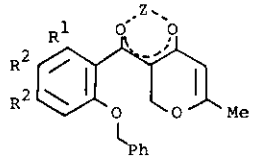
Synthesis of fulvic acid (9) was accomplished by a route involving a selective ozonization of (5a), obtained by a regioselective cyclization of (1a).

As a preliminary experiment, (5b), the basic skeleton in (9) was synthesized as follows. Treatment of (1b) with acidic condition (dil.HCl/THF or dil.H_2SO_4/HOAc/THF) afforded a single cyclization product (2b). Application of Fujita's debenzylation method ($Me_2S/BF_3 \cdot OEt_2$) to the BF_2-complex (3b) of the pyrone (2b) followed by acidic cyclization (conc.HCl/HOAc) led to (5b).

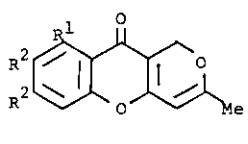
In the same manner, (1a) was converted into the propenyl derivative (5a), whose selective ozonization in the presence of a dye (Oil Violet) as a internal indicator followed by the reduction with methylsulfide produced the aldehyde (6). Selective demethylation of (7), derived from (6), was carried out by treatment with $AlCl_3$-Me_2S to give (8). Finally conversion of (8) into (9) was acieved by the hydration (5% HCl/Me_2CO, 55°C, 24 h.).



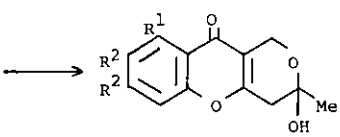
1a R^1=CH=CHMe, R^2=OMe
Y=H,$CH_2S(O)Me$
1b R^1=R^2=H, Y=CH_2 or H,$CH_2S(O)Me$



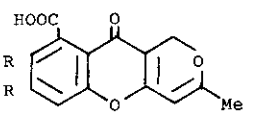
2a R^1=CH=CHMe, R^2=OMe, Z=H
2b R^1=R^2=H, Z=H
3a R^1=CH=CHMe, R^2=OMe, Z=BF_2
3b R^1=R^2=H, Z=BF_2



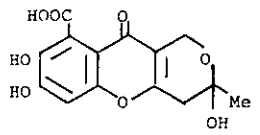
4a R^1=CH=CHMe, R^2=OMe
4b R^1=R^2=H



5a R^1=CH=CHMe, R^2=OMe
5b R^1=R^2=H
6 R^1=CHO, R^2=OMe



7 R=OMe
8 R=OH



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