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SYDOWIC ACID, A NEW METABOLITE FROM *ASPERGILLUS SYDOWI*

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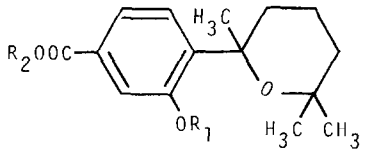
In the course of our investigation on fungal metabolites, we have isolated a new metabolite, which we have named sydowic acid (I), from *Aspergillus sydowi* (Bainier *et* Sartory) Thom *et* Church. We wish to report on the method of isolation and chemical structure of this metabolite.

Aspergillus sydowi was grown as a surface culture for 3 weeks at 24°C on a malt extract medium. The culture filtrate was stirred with activated charcoal and the adsorbed metabolites were eluted with acetone. After the evaporation of acetone, the residue was dissolved in benzene. The portion soluble in benzene was subjected to chromatography on a column of cellulose powder and the elution was carried out with water saturated ether to give a yellow gum. Crystallization of this gum from ether-hexane gave colorless needles, mp 151°C, $[\alpha]_D^{21}$-6.4° (c=1.1, $CHCl_3$). Found : C, 68.45, H, 7.56; MS m/e : 264 (M^+). Calcd. for $C_{15}H_{20}O_4$: C, 68.16; H, 7.63%, M.W., 264. UV λ_{max}^{EtOH} nm (ε) · 243 (8700), 296 (2800). IR ν_{max}^{KBr} cm^{-1} : 3230, 1685, 1580. This compound is soluble in aqueous sodium bicarbonate, and this gave a yellow color with bromophenol blue and a brown color with ethanolic ferric chloride. Its UV spectrum is closely similar to that of 2-hydroxy-*p*-toluic acid [UV λ_{max}^{EtOH} nm (ε) · 243 (8300), 295 (3000)]. The NMR spectrum of I in deuterochloroform showed three singlets at δ 0 95 (3H), 1.38 (3H) and 1.50 (3H) due to three tertiary methyl protons and multiplets at δ 1 5-1.8 (5H) and 2.2-2.6 (1H) The signals at δ 7.14 (1H, doublet, J=9 Hz), 7.57 (1H, doublet, J=2 Hz) and

7.60 (1H, doublet of doublets, J=2 and 9 Hz) were assigned to three aromatic protons. The signals at δ 9.37 (1H, singlet) and 11.01 (1H, broad) were disappeared on treatment with deuterium oxide. Acetylation of I gave a monoacetate (II), an oil, MS m/e : 306 (M^+). Its NMR spectrum showed a singlet at δ 2.33 (3H) due to the methyl protons of the phenolic acetyl group, and the IR spectrum showed a absorption band at 1775 cm^{-1}. Methylation of II gave a methyl ester (III), an oil, MS m/e : 320 (M^+). Its NMR spectrum showed a singlet at δ 3.85 (3H) due to methoxy protons and no signals disappeared on treatment with deuterium oxide. These results indicate the presence of 4-substituted 3-hydroxybenzoic acid in I.

Both the proton noise decoupled and off-resonance CW decoupled FT-^{13}C-NMR data of sydowic acid in deuterochloroform showed the presence of fifteen carbons in the molecule. Seven carbons of them were specified with one carbonyl carbon δ c (172.0 ppm) and six aromatic ring carbons distributed as three with attached proton (118.9, 121 3 and 124 6 ppm), one with oxygen (157.1 ppm) and two carbons with carbon (129 6 and 137 0 ppm). The remainder of the carbons was identified as two quaternary carbons bonded to oxygen (75.3 and 77.6 ppm), three methylene carbons (16 6, 33.8 and 36 7 ppm) and three methyl carbons (24.8, 31 3 and 31 9 ppm).

On the basis of these results, sydowic acid is represented by formula I.



(I) : R_1=R_2=H

(II) · R_1=$COCH_3$, R_2=H

(III) · R_1=$COCH_3$, R_2=CH_3