Tetrahedron Letters No.18, pp 1287-1288, 1965 Pergamon Press Ltd.
Printed in Great Britain.

DUCLAUXIN , A METABOLITE OF PENICILLIUM DUCLAUXI (DELACROIX)

S. Shibata, Y. Ogihara, N. Tokutake* and O. Tanaka
Faculty of Pharmaceutical Sciences, University of Tokyo, Japan

(Received 16 March 1965)

DUCLAUXIN is one of the metabolites of Penicillium duclauxi (Delacroix) grown on the Czapek-Dox medium. It forms colourless crystals (from benzene or acetone-ethanol), $C_{29}H_{22}O_{11}$, m.p. 230° (decomp.), $[\alpha]_D^{30}$ + 272.5° (c= 5.4% in $CHCl_3$). It dissolves in conc. H_2SO_4 with red colour, and gives a violet ferric reaction.

The UV spectral bands at 233 mμ (log ε 3.95) and 318 mμ (log ε 3.21), and the IR absorptions at 1650-1500 cm^{-1} suggested the presence of aromatic structure in the molecule of duclauxin.

The IR absorptions at 1710,1760 and 1690 cm^{-1} revealed the presence of lactone, ester and ketone groupings, and the band at 3300 cm^{-1} indicated the hydroxyl.

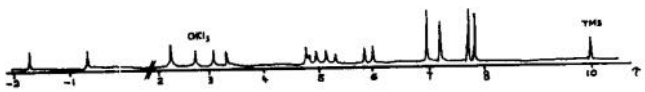
The n.m.r. spectrum of duclauxin showed the presence of $OCOCH_3$ (τ 7.87), 2 CH_3 (τ 7.78, 7.25), OCH_3 (τ 7.00), O-C(H)-C(H) (τ 4.90, 5.17 (doublets)), 2 tert.H (τ 6.00, 5.83), O-CH< (τ 4.78), 2 aromatic H (τ 3.32, 3.05), H-C(=O) (τ 2.23), and 2 OH (τ -0.75, -1.79).

On acetylation of duclauxin with acetic anhydride and pyridine, a diacetate, $C_{29}H_{20}O_9(OCOCH_3)_2$, m.p. 257°(decomp.) was obtained, and on bromination with dioxane dibromide and pyridine in tetrahydrofurane monobromoduclauxin, $C_{29}H_{21}O_{11}Br$, m.p. 260° (decomp.) was afforded. The n.m.r. signals of duclauxin at

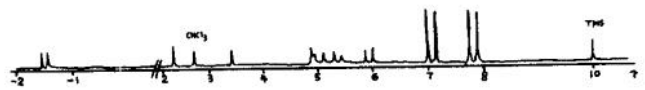
* Present address: Shionogi Research Laboratory, Shionogi & Co.Ltd.

τ - 0.75 and -1.79 dissapeared on acetylation, and that of τ 3.05 (an aromatic proton) was not observed in the monobromo derivative. The position of bromine substitution was indicated by the shift of signals of neighbouring OH ($\rightarrow\tau$-1.54) and CH_3 ($\rightarrow\tau$7.13) by the bromination of duclauxin.

It is noted that on treatment with ammonia, duclauxin was converted into an orange red crystalline N-containing compound named duclauxamine.



Duclauxin



Monobromoduclauxin 100 Mc.(in $CDCl_3$)

The stereochemical structure of duclauxin has been established by the X-ray analysis of crystals of monobromoduclauxin[1], and the IR absorption bands and the n.m.r. signals are assigned as being consistent with the structure.

Acknowledgements: We wish to thank Mr.S.Udagawa,National Institute of Hygienic Sciences for supplying mould strain, and Messrs M.Nishio, T.Takekoshi, and H.Maruyama for their co-operations. The n.m.r. spectra were measured by Miss Y. Shibamura,National Institute of Radiological Sciences, to whom our thanks are due.

Reference : 1) Y. Ogihara,Y.Iitaka, and S. Shibata: Tetrahedron Letters, No.18, 1289 (1965).