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STRUCTURE OF XANTHOMONADIN I, A NOVEL DIBROMINATED ARYL-POLYENE PIGMENT PRODUCED BY THE BACTERIUM XANTHOMONAS JUGLANDIS

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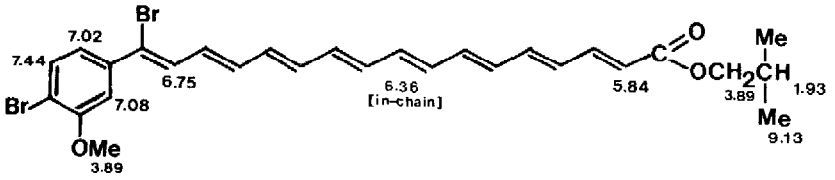
Only marine organisms are generally considered to command the capacity to concentrate, fix and incorporate bromine in organic compounds. The two reported exceptions to the marine connection involve a human spinal fluid component, 1-methylheptyl-γ-bromoacetoacetate[2], and the aromatic brominated polyene esters isolated by ourselves from the bacterial organism Xanthomonas juglandis strain XJ103[3,4], a pathogen of a terrestrial plant (walnut). These latter compounds were incompletely characterized and we now report the detailed structure of one component, xanthomonadin I (1), as determined by x-ray crystallographic methods.

Treatment of crude, cellular extracts of XJ103 containing pigment-lipid complexes[3] with strong base for a short time (10 min., R.T.) gave, in effect, transesterification products. Thus, $^{-}$OMe/MeOH or iso-$^{-}$OBu/iso-BuOH yielded mixtures of methyl and iso-butyl brominated polyene esters, respectively. The superior solubility characteristics of iso-butyl esters vs. the methyl esters facilitated structural studies.

Extractive isolation of iso-$^{-}$OBu treated extracts of XJ103 followed by Si gel column chromatography (developed with mixtures of petroleum ether-benzene and benzene-$CHCl_3$) gave one major and several minor pigments. The major and least retentive pigment, the orange-red iso-butyl xanthomonadin I (1; *ca. 1 mg from 540 g wet cells), crystallized from dilute acetone* solution; m.p. 169-170°. The following physical properties were recorded: λ_{max} (423), 445 (ε=147,500), 473 (ε=122,900) in acetone; (430), 453 (ε=131,500), 482 (ε=109,500) in $CHCl_3$; IR (KBr) 3010, 2995, 1708, 1625, 1602, 1575, 1490, 1398, 1382, 1240, 1233, 1215, cm^{-1}; m/e 572/574/576 (M^+, $C_{28}H_{30}Br_2O_3$); δ($CDCl_3$), see assignments on structure 1.

Isobutyl xanthomonadin I [1; isobutyl 17-(4-bromo-3-methoxyphenyl)-17-bromo-heptadeca-2,4,6,8,10,12,14,16-octaenoate] crystallizes in the monoclinic space group $P2_1/c$ with cell constants a = 42.46, b = 7.77, c = 7.87 Å, β = 92.47°, four molecules in the unit cell. The intensities of 2571 reflections (Cu Kα, max 2θ = 100°) were measured at 85 K on a Picker automatic diffractometer. The crystals were extremely thin and of poor quality, resulting in irregular and broad (>2°) ω scans. In order to enhance counting statistics, the intensity measurements were performed as 1.5° ω scans (1° min^{-1}) over the most intense part of the peaks.

The structure was solved by heavy atom Patterson and Fourier methods. Refinement is complicated by disorder, with about 20% of the molecules related to the major structure through a non-crystallographic mirror plane. Details will be reported elsewhere[5].



ISOBUTYL XANTHOMONADIN I (1)

Oxidation of 1 by $KMnO_4$ in tert-BuOH-H_2O followed by esterification gave the expected methyl 4-bromo-3-methoxybenzoate, which after comparative chromatography (GLC and TLC) could not be separated from authentic material and thus supports the structure assigned by x-ray crystallographic methods.

Xanthomonadin I (1) and related compounds[6] have now been identified in all studied Xanthomonas species and pathotypes[7].

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2. Yanagisawa, I. and Yoshikawa, H., Biochim. Biophys. Acta 329 (1973) 283.
3. Andrewes, A. G., Hertzberg, S., Liaaen-Jensen, S. and Starr, M. P., Acta Chem. Scand. 27 (1973) 2383.
4. Andrewes, A. G., Acta Chem. Scand. 27 (1973) 2574.
5. Hope, H. and Shepherd, J., Acta Crystallogr. To be published.
6. Andrewes, A. G., Jenkins, C. L. and Starr, M. P., Eur. J. Biochem. To be published.
7. Starr, M. P., Jenkins, C. L., Bussey, L. B. and Andrewes, A. G., Arch. Microbiol. To be published.