A Terpenoid 4,7-Thianaphthenequinone from an Extremely Thermophilic and Acidophilic Micro-organism

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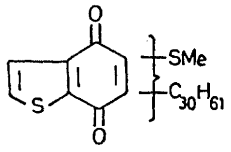
Summary The occurrence of a terpenoid benzo[*b*]thiophen-4,7-quinone (**1**) in an acidophilic bacterium growing at up to 89 °C is reported; this is the first occasion on which a thianaphthenequinone has been found in natural source.

Caldariella acidophila is a bacterium of a novel genus of extremely thermophilic and acidophilic character isolated from natural habitats in the volcanic area of Naples, and has optimal growth at temperatures of 75—90 °C and pH 3·5—1·5. We have already reported the physiological,[1] ultrastructural,[2] and chemical[3] data for this organism. Ester lipids are totally absent, and all the major lipids are based on a cyclic 1,2-diether of glycerol with a bidentate C_{40} isoprenoid unit.[3]

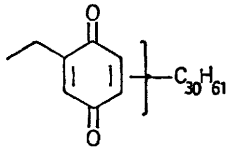
We now report the isolation of a terpenoid benzo[*b*]-thiophen-4,7-quinone (**1**), the first occasion on which such a quinone chromophore has been found in a natural source.

The total lipid extract ($CHCl_3$–MeOH) from 200 g of liophylized cells was treated with light petroleum and the soluble material, after chromatography on silica, gave 110 mg of an orange-red oil (0·055% of the dry weight of cell). It analysed for $C_{39}H_{66}O_2S_2$ (elemental analysis and high resolution mass spectrometry), and showed u.v. absorptions at 241, 283, 333, and 471 nm (log ϵ 4·11, 3·90, 3·70, and 3·07 in MeOH) and i.r. bands (liquid film) at

1668 and 1647 cm^{-1}, closely resembling those of 1,4-naphthaquinones.[4] It has typical redox properties and formed a leucodiacetate, M^+ *m/e* 716, ν_{max} 1770 cm^{-1}. The n.m.r. spectrum showed two low-field protons at δ 7·5 (ABq, *J* 5 Hz), and a methyl singlet at δ 2·62; the remaining part of the spectrum corresponded to a C_{30} saturated isoprenoid chain. Oxidation with alkaline H_2O_2 followed by methylation with diazomethane, afforded a major compound giving in the mass spectrum M^+ at *m/e* 480 corresponding to the methyl ester of a saturated C_{31} acid.



(1)



(2)

As the molecular formula of the parent compound is $C_{39}H_{66}O_2S_2$ the molecule must contain a $C_{30}H_{61}$ chain linked to a $C_9H_5S_2O_2$ unit which can be formulated as a benzo[*b*]thiophen-4,7-quinone with an MeS substituent as shown in (**1**), in agreement with above spectral data, when compared with those of synthetic benzo[*b*]thiophen-quinones.[5]

Desulphurization with Raney nickel[6] led to an ethyl-C_{30}-alkyl-disubstituted-1,4-benzoquinone (**2**).[4]

Structural studies on (**1**), concerning the relative positions of the ring substituents and the exact nature of the C_{30} isoprenoid chain, continue. Meanwhile the basic structure (**1**), which is in a sense related to vitamin K_2's, suggests a possible respiratory function for this quinone. Fieser and his co-workers[7] found that the reduction potentials of the benzo[*b*]thiophenquinones are *ca.* 75 mV higher than for the corresponding naphthaquinones and thus the possible implication of this quinone in the electron transport system of *Caldariella acidophila* is even more interesting.

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[1] M. De Rosa, A. Gambacorta, and J. D. Bu'Lock, *J. Gen. Microbiol.*, 1975, **86**, 156.
[2] G. Millonig, M. De Rosa, A. Gambacorta, and J. D. Bu'Lock, *J. Gen. Microbiol.*, 1975, **86**, 165.
[3] M. De Rosa, A. Gambacorta, L. Minale, and J. D. Bu'Lock, *J.C.S. Chem. Comm.*, 1974, 543.
[4] R. H. Thomson, 'Naturally Occurring Quinones,' 2nd edn., Academic Press, New York and London, 1971, p. 39.
[5] I. Baxter and B. A. Davis, *Quart. Rev.*, 1971, **25**, 239; C. J. P. Spruit, *Rec. Trav. Chim.*, 1962, **81**, 810.
[6] F. F. Blicke and D. G. Sheets, *J. Amer. Chem. Soc.*, 1949, **71**, 4010.
[7] L. F. Fieser and D. P. Ames, *J. Amer. Chem. Soc.*, 1927, **49**, 2604; L. F. Fieser and R. G. Kennelly, *ibid.*, 1935, **57**, 1611.