X-Ray Crystal and Molecular Structure of 3β-Acetoxy-6,7-epidithio-19-norlanosta-5,7,9,11-tetraene, the Stable Dithiete Tautomer of a Dithio-*o*-quinone

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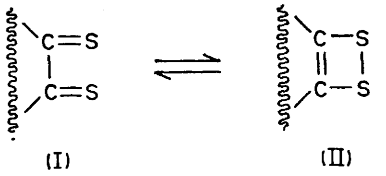
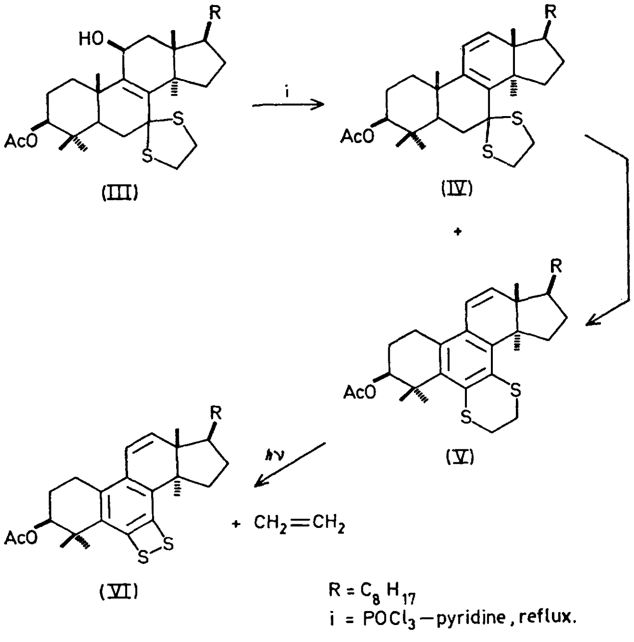
Summary The preparation and structure determination of the title compound, a representative of a novel structural class, is described.

There are few reports of the preparation of α-dithiones (I) or their valence tautomers 1,2-dithietes (II)[1] and dithioquinones are unknown. We now report the preparation and structure determination of the stable, crystalline dithiete tautomer of a dithio-*o*-quinone incorporated within the nucleus of a lanostane triterpenoid.



Treatment of 3β-acetoxy-7,7-ethylenedithio-5α-lanost-8-en-11β-ol (III)† with phosphoryl chloride in pyridine under reflux gave the expected 8,11-diene (IV) and, with prolonged reaction times, increasing amounts of a colourless compound, $C_{33}H_{48}O_2S_2$, m.p. 161—163°, $[\alpha]_D + 45°$. N.m.r. spectroscopy indicated the loss of a methyl group and together with the u.v. spectrum [λ_{max} 263 (ϵ 14500) and 309 nm (12500)], suggested that this product was the 2,3-dihydro-1,4-benzodithiine (V). Photolysis of (V) in n-heptane at −20° using a medium pressure mercury vapour lamp brought about a rapid and quantitative conversion into a stable, yellow crystalline compound, $C_{31}H_{44}O_2S_2$, m.p. 168—170°, $[\alpha]_D + 60°$, λ_{max} 249 (ϵ 24000), 253, (24000) and 300 nm (12100). Ethylene was also formed (g.l.c. analysis of the derived dibromide). Unequivocable identification of the photolysis product as the dithiete (VI) was achieved by *X*-ray analysis.



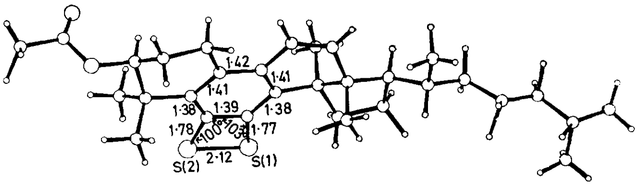


Figure. Circles represent in order of decreasing size, S, O, C, H.

Crystals of (VI) separated from 1 : 1 dichloromethane–methanol as yellow, needle-shaped parallelepipeda: $P2_1$, $a = 20{\cdot}1889(9)$, $b = 11{\cdot}0705(5)$, $c = 6{\cdot}4951(3)$ Å, $\beta = 90{\cdot}578(2)°$, $Z = 2$. Intensities of 2605 reflections with $\sin\theta/\lambda < 0{\cdot}60$ were measured on a Siemens diffractometer (A.E.D.) with Cu-K_α radiation. Among the data, 243 reflections for which $I < 2{\cdot}58\ \sigma(I)$ were classed as unobserved. The structure (Figure) was solved by the heavy-atom technique, and refined by full-matrix least squares to $R = 3{\cdot}4\%$. The absolute stereochemistry was determined from the anomalous dispersion of the sulphur atoms, and was as expected.

The more important bond lengths and angles are shown in the Figure. The S–C–C angles and the S–S distance indicate bonding between the two sulphur atoms. This is supported by a Raman band at 486 cm.$^{-1}$ [2] Ring B is planar (σ = 0·01 Å), and the deviations of S(1) and S(2) from this plane are 0·00 and 0·05 Å respectively. There are no abnormal intermolecular contacts, the shortest such S . . . . . S distance being about 10 Å.

The exceptional stability of the dithiete (VI) must, at least in part, be attributed to the steric protection afforded it by the host molecule.

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† The preparation and other reactions of this compound will be described in a full paper. Satisfactory analytical and spectroscopic data were obtained for all new compounds.

[1] W. Kusters and P. de Mayo, *J. Amer. Chem. Soc.*, **1974**, **96**, 3502 and references therein.

[2] J. Cymerman and J. B. Willis, *J. Chem. Soc.*, 1951, 1332.