Oxidation of dehydro-L-ascorbic acid phenylosazone

The red dehydro-L-ascorbic acid phenylosazone was recently shown[1] to exist in the 1,5-lactone bis(phenylhydrazone) form (**1a**). We have found that mild oxidizing agents, such as cupric chloride and iodine, convert this osazone into a yellow dehydro-osazone (**2a**). The u.v. spectrum of **2a** shows maxima at 205, 219, 239, 280, and 366 nm, and its i.r. spectrum has a lactone band at 1720 cm^{-1} in exactly the same position as that of the red osazone **1a**, suggesting that the lactone ring remains unaffected during the oxidation. Compound **2a** gave, on acetylation, a yellow mono-*O*-acetyl derivative (**2b**) which showed a broad, unresolved band at 1740 cm^{-1} (ester and lactone). The n.m.r. spectrum of the yellow acetate **2b** (see Fig.1) was quite similar to that of the

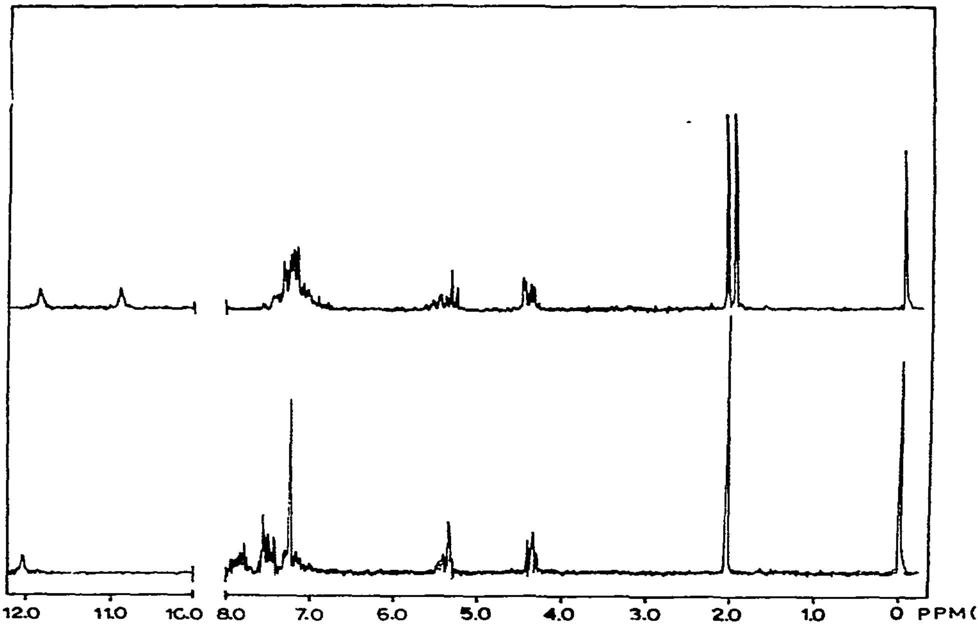


Fig.1. N.m.r. spectrum in chloroform-*d*. Upper graph (**1b**); lower graph (**2b**).

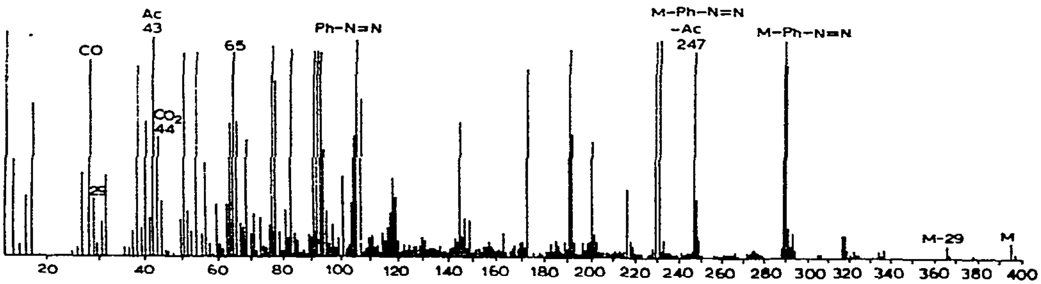
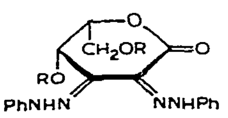


Fig.2. Mass spectrum of **2b**.

red 4,6-di-*O*-acetyl-dehydro-L-ascorbic acid phenylosazone (**1b**), except for the fact that it showed one acetyl group instead of two, and one imino proton instead of two. The methylene group of C-6 was at 5.64 followed at τ 4.67 and τ 4.56 by the C-4 and C-5 protons. The mass spectrum (see Fig.2) of **2b** agreed with a molecular weight of 394.5; it showed major peaks at 105 and M-105 due to the splitting of the Ph-N=N group, and a peak at 43 and M-105-43 due to the further splitting of the acetyl group. In addition, it showed the 65 peak of *N*-substituted anilines, and the 44 (CO_2) and 28 (CO) peaks, all of which agree with the assigned structure (**2b**), namely, 4-*O*-acetyl-3,6-anhydro-3-phenylazo-L-*xylo*-hexulosono-1,5-lactone phenylhydrazone, in which the primary hydroxyl on C-6 of the osazone precursor has cyclized with C-3, with subsequent oxidation to phenylazo of the hydrazo group formed.



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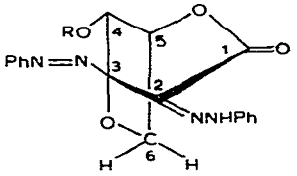

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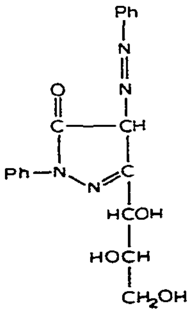

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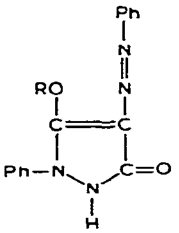

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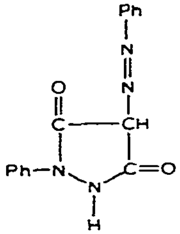

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(a, R=H; b, R=Ac)

That the cyclization of the primary hydroxyl group involved C-3, not C-2, was apparent when the dehydro-osazone (2a) was treated with alkali, and the mixture was acidified. Under these conditions, the parent, red osazone (1a) yields 1-phenyl-4-phenylazo-3-(L-*threo*-1,2,3-trihydroxypropyl)pyrazolin-5-one^2 (3a); the dehydroderivative (2a), on the other hand, cyclized to a yellow compound (4a), which proved to be the enol form of the known 1-phenyl-4-phenylazopyrazolidin-3,5-dione (5). The presence of the carbonyl oxygen atom on C-3 of 4a is strongly indicative of the involvement of the C-3 hydrazone residue of 2a in anhydro-ring formation, especially since, sugar under similar treatment, phenylosazones yield^3 glyoxal bis(phenylhydrazone) with no oxygen atom on C-2.

The yellow cyclization product 4a showed one carbonyl band at 1685 cm^{-1}, and, on acetylation, it yielded a mono-acetate (4b) having a carbonyl band at 1710 (CONH) and at 1740 cm^{-1} (OAc); its n.m.r. spectrum revealed the *O*-acetyl protons at τ 7.33, deshielded by the heterocyclic ring; the phenyl protons appeared at τ 2.62, and the deuterable, imino proton showed at τ −2.50. The mass spectrum of the acetate agreed with a molecular weight of 322, and showed many of the peaks of the parent **2b**, such as the Ph-N=N and M-Ph-N=N, the Ac at 43, etc., all of which agree with structure **4b**. Final proof of this structure was reached by acetylation of the known 1-phenyl-4-phenylazopyrazolidine-3,5-dione[4] (**5a**); this tautomer of **4a**, the i.r. spectrum of which possesses two carbonyl bands (at 1745 and 1720 cm^{-1}), gave, on acetylation, the same acetyl derivative **4b** as the one obtained from **4a**.

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