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Preliminary communication

Semicarbazones derived from dehydro-L-ascorbic acid*

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In continuation of investigations[1] on the chemistry of nitrogenous derivatives of L-ascorbic acid[1–6] (1), we now report the synthesis of some new derivatives of this class of compound. Also, a case of acetalation occurring during the periodate oxidation of semicarbazone of 3-(L-*threo*-glycerol-1-ylcarbonyl)-2-quinoxalinone (2) is described; if this unexpected acetalation (2 → 4) could be successfully applied when the aldehyde resulting from the periodate oxidation of 1,2-glycols is unstable, it would constitute a novel method gor protection thereof.

The reaction of the oxidation product of 1 with *o*-phenylenediamine, followed by treatment with semicarbazide, afforded 2. Oxidation of 2 with periodic acid in 1,4-dioxane–methanol, followed by treatment with semicarbazide, did not give the anticipated aldehyde 1-semicarbazone, that of 3-(glyoxal-1-yl)-2-quinoxalinone (3). Instead, a product (m.p. 230°) was obtained whose elemental analysis agreed with the formula $C_{13}H_{15}N_5O_4$. Its structure was assigned on the basis of its infrared spectrum (no –CH=O absorption), as well as its ^{1}H-n.m.r. spectrum. The latter exhibited a singlet at δ 3.10 (6 H), attributed to the presence of two equivalent methoxyl groups, and a singlet at δ 5.30 (1 H), resonating at a field position incompatible with an aldehydic proton. The chemical shift of this proton indicated its attachment to a carbon atom bearing two methoxyl groups. In addition, there were three singlets, at δ 6.40, 10.00, and 12.46, with intensity ratios of 2:1:1, attributed to the four protons situated on the nitrogen atoms. The four aromatic protons appeared as a multiplet between δ 7.17 and 8.05. These data, and the method of preparation, led to assignment of the product as the dimethyl acetal (4) of 3.

On the other hand, periodate oxidation of 2 suspended in an aqueous solution of sodium metaperiodate afforded a product (m.p. 257–260°) different from 4. Attempted purification thereof by crystallization from alcoholic solvents led to its partial transformation into another product whose elemental analysis indicated either that

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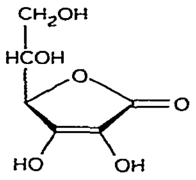

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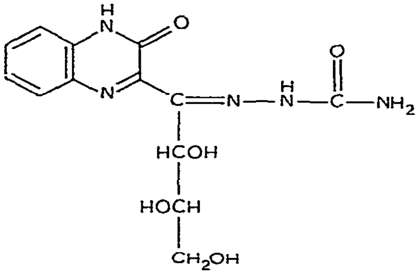

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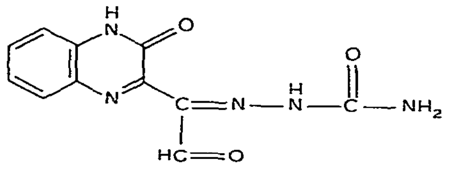

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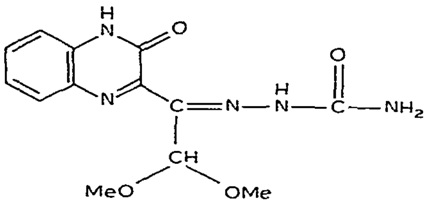

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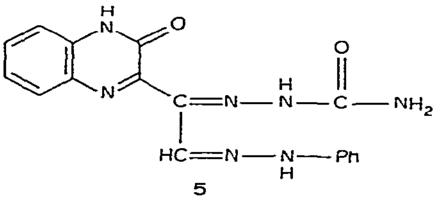

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partial acetalation had occurred or that alcohol of crystallization was present. However, the ^{1}H-n.m.r. spectrum of the crude, metaperiodate-oxidation product of **2**, showed, in addition to the four protons on the nitrogen atoms, at δ 6.93 (2 H), 11.00, and 12.53, a singlet at δ 9.53 for an aldehydic proton, as well as four aromatic protons (multiplet) between δ 7.10 and 7.83. These findings are in agreement with structure **3** for the oxidation product. Moreover, whereas compound **4** did not react with phenylhydrazine, **3** reacted therewith to give the expected hydrazone, namely, 3-(2-phenylhydrazono-1-semicarbazonoglyoxal-1-yl)-2-quinoxalinone (**5**).

The formation of acetal **4** from **2** is, presumably, a consequence of the reaction of **3**, resulting from the periodate oxidation of **2**, with the methanol in the strongly acidic, anhydrous methanol–1,4-dioxane solution, conditions favorable to acetal formation.

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