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Note

Reaction of dehydro-L-ascorbic acid analogues with *o*-phenylenediamine*

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The products of reaction of dehydro-L-ascorbic acid with *o*-phenylenediamine have been reviewed[1,2] and we have found a close similarity of their structures with those obtained from its analogue dehydro-D-isoascorbic acid.

In 1964, Dahn and Moll[3] assigned to the products of reaction of dehydro-L-ascorbic acid and its aryl analogues with 2 equiv. of *o*-phenylenediamine, a structure **5** rather than **4** and **7** which were given in earlier reports[4]. However, contradictory reports[5,6] on the structure of the reaction product of the aryl analogue of **3** have appeared, and structure **4** was assigned. Since such products showed bands at 1680–1690 cm^{-1} for amide groups, they should be formulated as **5**, and not **4** or **7**, because **4** should show a lactone carbonyl absorption whereas **7** should not show any carbonyl absorption. Moreover, such structures as **6** and **8** formed from **3** could be identified by elemental analysis and i.r. absorption for a lactone carbonyl in the former, and the formation of a red phenylhydrazone from the latter.

We have described the scope of synthesising *C*-nucleoside analogues possessing the structural features of L-ascorbic acid[7–9]. Although the imino group of 2,5-dihydro-5-imino-2-(2-phenyl-1,2,3-triazol-4-yl)furan-3,4-diol (**1**) could be cleaved with nitrous acid, simultaneous oxidation of the enediol system also occurred to give 2,3-dioxo-4-(2-phenyl-1,2,3-triazol-4-yl)-4-butanolide (**3**). Reduction of **3** afforded 2,3-dihydroxy-4-(2-phenyl-1,2,3-triazol-4-yl)-2-buten-4-olide (**2**).

The reaction of **3** with 2 mole of *o*-phenylenediamine afforded a product ($C_{24}H_{19}N_7O_2$) which had an i.r. band at 1640 cm^{-1} for an amide group. The structure **5** assigned[9] was confirmed by its mass-spectral fragmentation pattern shown in Scheme 1.

EXPERIMENTAL

General methods. — Melting points were determined with a Kofler block apparatus and are uncorrected. I.r. spectra were recorded with a Unicam SP 1025

*Heterocycles from Carbohydrate Precursors, Part 29. For Part 28, see ref. 1.
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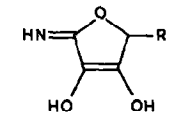

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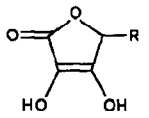

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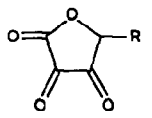

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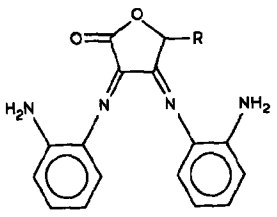

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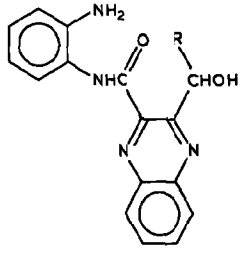

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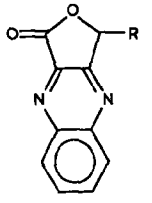

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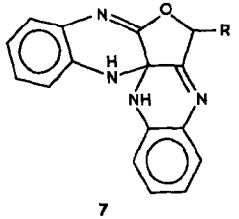

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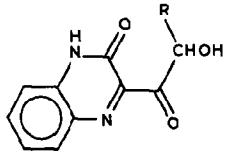

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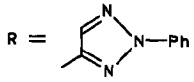


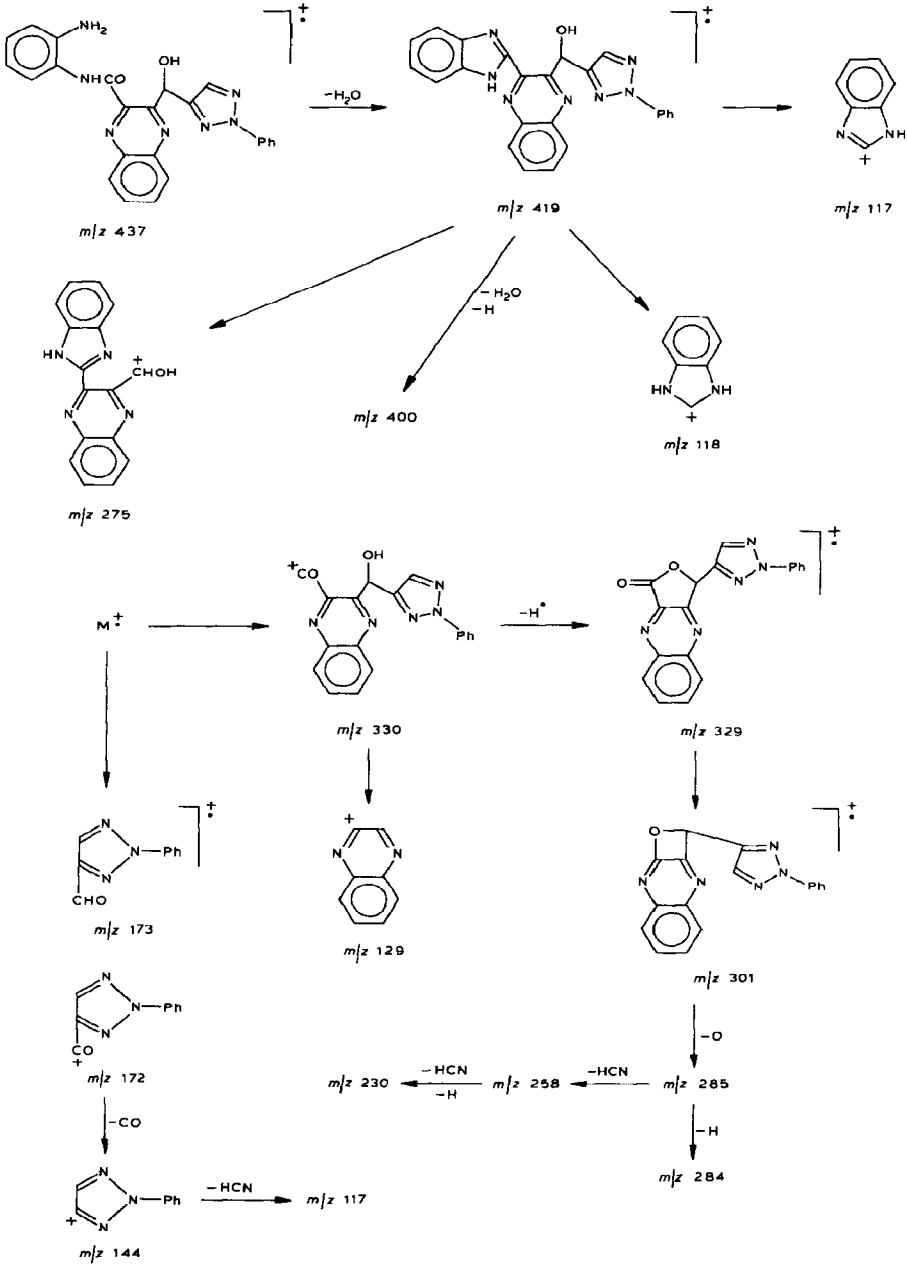
spectrometer. Microanalyses were performed in the Chemistry Department, Faculty of Science, Cairo University. The e.i. mass spectrum was obtained with an A.E.I. MS 902 instrument.

Compound **1**, prepared from 4-formyl-2-phenyl-1,2,3-triazole, had m.p. 160°; lit.[7] m.p. 156–158°; lit.[8] m.p. 184°. 2,3-Dioxo-4-(2-phenyl-1,2,3-triazol-4-yl)-4-butanolide (**3**), prepared[7] by the action of nitrous acid on **1**, had m.p. 204°; lit.[7] m.p. 207°; lit.[8] m.p. 132°.

2,3-Dihydroxy-4-(2-phenyl-1,2,3-triazol-4-yl)-2-buten-4-olide (**2**). — A solution of **3** (0.5 g) in methanol (15 mL) was treated with dry hydrogen sulphide at 20° for 10 h and then concentrated to dryness *in vacuo*. The product **2** crystallised from ethanol as colourless needles, m.p. 145°; ν_{max}^{KBr} 3300 (OH) and 1800 cm^{-1} (OCO).

Anal. Calc. for $C_{12}H_9N_3O_4$: C, 55.6; H, 3.5; N, 16.3. Found: C, 55.3; H, 3.5; N, 16.2.

3-[*Hydroxy(2-phenyl-1,2,3-triazol-4-yl)methyl*]*quinoxaline-2-carboxylic acid* o-*aminoanilide* (**5**). — A solution of **3** (0.5 g) in methanol (10 mL) was treated with



Scheme 1. Mass spectral fragmentation pattern of 5

a solution of *o*-phenylenediamine (0.8 g) in methanol (10 mL), and the mixture was boiled under reflux for 10 min. The product (83%) was collected, washed with ethanol, dried, and crystallised from ethanol to give **5** as yellow needles, m.p. 225°; ν_{max}^{KBr} 3450 (OH), 3320, 3220 (NH), 1640 cm^{-1} (OCN). Mass spectrum: *m/z* 438 (2%), 437 (3), 419 (7), 388 (3), 330 (8), 329 (20), 301 (2), 300 (1), 285 (9), 284 (10), 272 (3), 264 (8), 263 (7), 258 (5), 246 (6), 235 (10), 230 (6), 219 (3), 210 (2), 196 (3), 181 (4), 172 (10), 163 (5), 156 (7), 144 (10), 134 (21), 129 (43), 117 (11), 108 (18), 102 (60), 91 (88), 80 (58), 77 (100).

Anal. Calc. for $C_{24}H_{19}N_7O_2$: C, 65.9; H, 4.4; N, 22.4. Found: C, 65.6; H, 4.3; N, 22.6.

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