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Preliminary communication

Bromodeoxy-isoascorbic acid and derivatives thereof

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Bromodeoxy sugar derivatives[1] are of potential synthetic value, in addition to the biological significance of some of them. The synthesis of 6-bromo-6-deoxy-L-ascorbic acid was reported in a patent[2] using hydrogen bromide in formic acid, and recently[3] using hydrogen bromide in acetic acid. The latter reagent has found wide application in the carbohydrate field, as shown by Bock and Pedersen[4].

In continuation of our work on the synthesis and reactions of L-ascorbic acid analogs[5], the reaction of isoascorbic acid (**1**) with hydrogen bromide in acetic acid was performed, followed by deacetylation to give **3** (*via* **2**), which, on treatment with phenylhydrazine, afforded a mixture of products from which was isolated compound **6**, found to have a molecular formula of $C_{18}H_{16}N_4O_3$; its infrared spectrum showed a band at 1740 cm^{-1}, and, on acetylation, it afforded a monoacetyl derivative, **7**, $C_{20}H_{18}N_4O_4$, m.p. 245–248°, whose n.m.r. spectrum showed the presence of only one acetyl group and one imino proton, at δ 1.94 and 11.44, respectively. Reaction of **6** with alkali afforded a product (m.p. 165–166°) whose elemental analysis agreed with that calculated for the hydrated form of **6**, and which, on acetylation, afforded the same acetate as that obtained from **6**. Consequently, the reaction of **3** with phenylhydrazine may give the bis(hydrazone) **5** that undergoes a cyclization of the hydrazone residue *via* nucleophilic displacement of the bromine atom. The L-*threo* analog of **5** was prepared from 6-bromo-6-deoxy-L-ascorbic acid[6], and its cyclization could be anticipated to occur, depending upon the reaction conditions. Thus, an attempted displacement of the 6-sulfonyloxy group of 6-*O*-*p*-tolylsulfonyl-L *threo*-2,3-hexodiulosono-1,4-lactone 2,3-bis(phenylhydrazone)[7] with iodine resulted in its cyclization into the L-*threo* analog of **6**, instead of formation of the corresponding 6-iodo derivative.

When 3-(D-*erythro*-glycerol-1-yl)-1-phenyl-4,5-pyrazoledione 4-(phenylhydrazone) (**8**) was allowed to react with hydrogen bromide in acetic acid, a product, namely, **9**, was isolated whose elemental analysis and mass spectrum showed a molecular formula of $C_{20}H_{18}Br_2N_4O_3$, indicating the absence of two of the three hydroxyl groups and acetyla-

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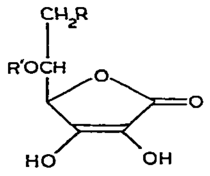
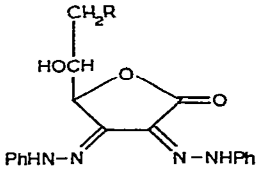
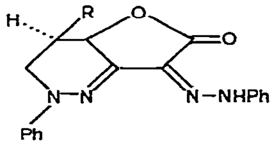


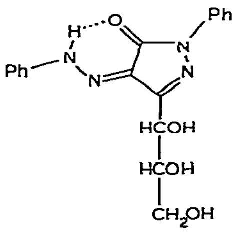
1 R =OH, R'=H
2 R =Br, R'=Ac
3 R= Br, R'= H



4 R =OH
5 R = Br



6 R = OH
7 R = OAc



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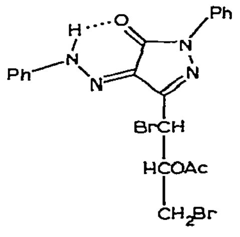

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tion of one. This was confirmed spectroscopically; the i.r. spectrum showed the presence of OAc and OCN groups at 1745 and 1665 cm^{-1}, respectively. The n.m.r. spectrum of **9** showed the presence of one acetyl group, at δ 2.19. The pronounced, high-field shift of H-1 (δ 5.5, d, 1 H) and H-3 (δ 3.74, 2 q, 2 H) of the glycerol-1-yl side-chain in **9** compared to those of the corresponding protons on carbon atoms bearing acetoxyl groups indicated their attachment to the two carbon atoms bearing bromine atoms, in addition to the situation of H-2 (δ 5.92, m, 1 H), indicating the presence of an acetoxyl group on that carbon atom. Moreover, the proposed mechanism for the bromination, using hydrogen bromide in acetic acid, confirms such assignments, and that the reaction occurs *via* a 1,3-dioxolan-2-ylium ion intermediate.

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