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Preliminary communication

Bromodeoxy analogs of some acyclic-sugar *C*-nucleosides

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The role of carbohydrates as precursors for the synthesis of nitrogen heterocycles has been investigated in our laboratory[1,2]. The potentiality of bromodeoxy sugars in synthesis, and the chemotherapeutic value of bromodeoxypolyols[3,4] and *C*-nucleosides[5,6], drew our attention to the synthesis of the bromodeoxy derivatives of some acyclic *C*-nucleosides.

Treatment of 3-(L-*threo*-glycerol-1-yl)-1-phenyl-4,5-pyrazoledione 4-(phenylhydrazone) (**1**) with hydrogen bromide in acetic acid did not give the corresponding monobromodeoxy derivative **4**, but a product (m.p. 202–204°) was obtained in high yield whose elemental analysis and mass-spectral data indicated its formulation as $C_{20}H_{18}Br_2N_4O_3$, and it is given the structure 3-(2-*O*-acetyl-1,3-dibromo-1,3-dideoxy-L-*erythro*-glycerol-1-yl)-1-phenyl-4,5-pyrazoledione 4-(phenylhydrazone) (**5**). On the other hand, compound **4** was prepared from 6-bromo-6-deoxy-L-ascorbic acid[7] (**9**) that upon reaction with phenylhydrazine gave the new 6-bromo-6-deoxy-L-*threo*-2,3-hexodiulosono-1,4-lactone 2,3-bis(phenylhydrazone) (**8**) and 3-(3-bromo-3-deoxy-L-*threo*-glycerol-1-yl)-1-phenyl-4,5-pyrazoledione 4-(phenylhydrazone) (**3**); on acetylation, **3** gave the desired compound **4** (m.p. 131–132°). The structure of the compounds was deduced from the spectral data; thus, the infrared spectra of compounds **1**–**5** showed a band at 1660 cm^{-1}, characteristic for the OCN of the pyrazoledione ring, whereas **8** (which may exist in the azohydrazino structure **10**, analogous to that recently proposed[8] for the L-ascorbic acid derivative) showed a band at 1725 cm^{-1} due to the OCO of the lactone ring.

For compounds **4** and **5**, the position of the bromine atoms was deduced from comparative study of their ^{1}H-n.m.r. spectra with that of 1-phenyl-3-(1,2,3-tri-*O*-acetyl-L-*threo*-glycerol-1-yl)-4,5-pyrazoledione 4-(phenylhydrazone)[9] (**2**). Compounds **3** and **4** were derived from a compound of known structure, namely, **9**, in which the bromine atom is on C-6, and, consequently, it is on C-3 of the side chain in **3** and **4**.

The chemical shifts of H-2 in **2**, **4**, and **5** are similar, at δ 5.79–5.90, indicating their similar attachment to the carbon atom bearing the acetoxyl group. Consequently,

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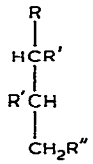
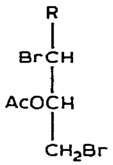


1 R′ = R″ = OH

2 R′ = R″ = OAc

3 R′ = OH, R″ = Br

4 R′ = OAc, R″ = Br



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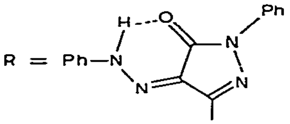

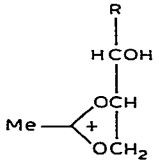

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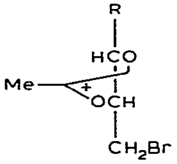

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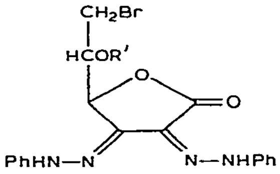
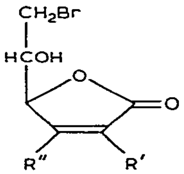


8 R′ = H



9 R′ = R″ = OH

10 R′ = NHNHR, R″ = NNPh

it may be concluded that the two bromine atoms in **5** are on C-1 and C-3 of the glycerol-1-yl side chain. This conclusion was supported by the data on the chemical shift of the doublet of H-1, appearing at δ 5.42, which is more shielded than H-2, whereas that proton doublet was more deshielded than H-2 in **2** and **4**, which appeared at δ 6.32 and 6.41, respectively.

The introduction of the bromine into these vicinal diols, using HBr—HOAc, occurred, *via* a 1,3-dioxolan-2-ylium ion intermediate, to give a *trans* bromoacetate. Consequently, the bromine atom in **5** may be introduced *via* the intermediate **7**, that derived from **6**, affording the *erythro* derivative.

In conclusion, this approach offers the potentiality of applying this procedure for the preparation of bromodeoxy derivatives of acyclic *C*-nucleosides.

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