Tetrahedron Letters No.14, pp. 1479-1482, 1966. Pergamon Press Ltd.
Printed in Great Britain.

BIS(2,3:5,6-DI-O-ISOPROPYLIDENE-D-MANNITOL) ORTHOCARBONATE

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(Received 17 January 1966)

We wish to report the isolation and identification of a novel orthocarbonate derivative of a sugar, the structure of which has two units of 2,3:5,6-di-O-isopropylidene-D-mannitol commonly bonded through the oxygen atoms at C-1 and C-4 to a carbon atom.

We have reported (1) that bis(1,2-O-isopropylidene-3-O-thiocarbonyl-α-D-glucofuranose) disulfide undergoes a rearrangement-fragmentation on standing in pyridine to give equimolar amounts of 1,2-O-isopropylidene-α-D-glucofuranose, 1,2-O-isopropylidene-α-D-glucofuranose 5,6-thionocarbonate, carbon disulfide, and free sulfur. In further studies on the behavior of the bis(O-thiocarbonyl) disulfide grouping, bis(2,3:5,6-di-O-isopropylidene-1-O-thiocarbonyl-D-mannitol) disulfide (I) was prepared. In pyridine I readily underwent decomposition to form 2,3:5,6-di-O-isopropylidene-D-mannitol, carbon disulfide, free sulfur, and crystalline bis(2,3:5,6-di-O-isopropylidene-D-mannitol) orthocarbonate (II), m.p. 246-247°. No thionocarbonate derivative could be isolated from the rearrangement mixture. The structure of II was formulated on the basis of the following experimental findings. Elemental analysis gave: C, 56.6; H, 7.6 ($C_{25}H_{40}O_{12}$ requires: C, 56.4; H, 7.5 of formula weight 532). Molecular-weight determination by the Rast method gave 520, whereas the

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mass spectrum (2) showed a high mass peak at 532 (FIG. 1). DeJongh and

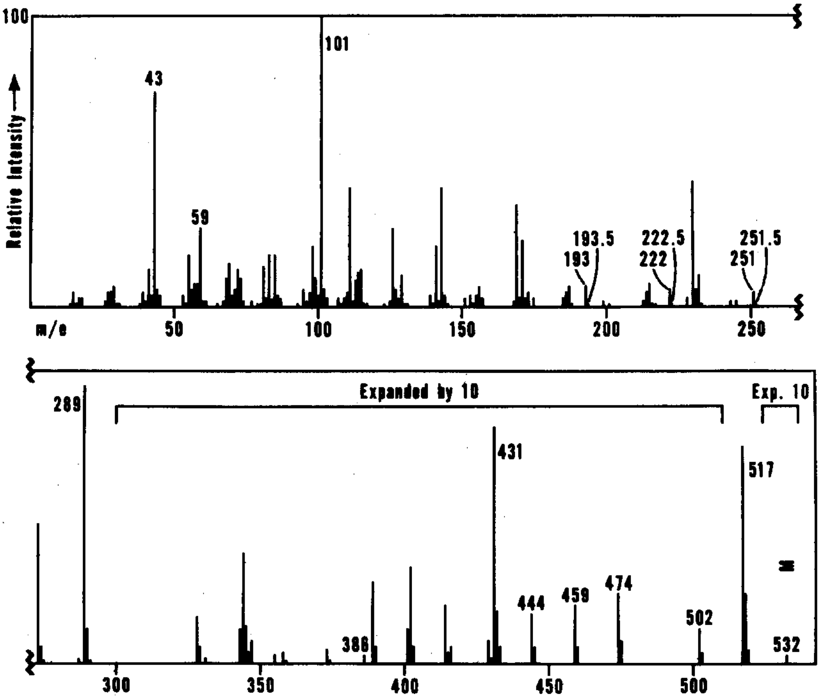
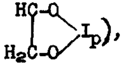
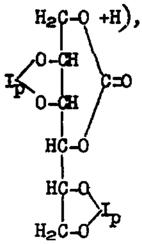
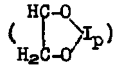


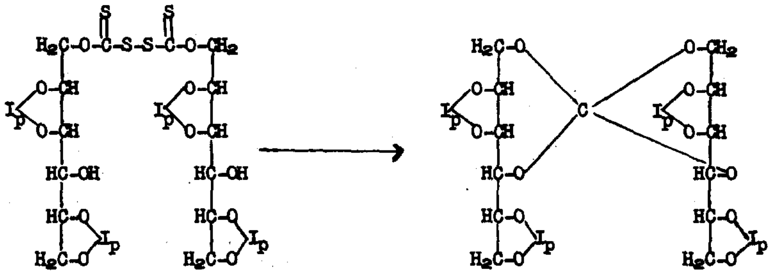
FIG. 1. Mass spectrum of bis(2,3:5,6-di-*O*-isopropylidene-*D*-mannitol) orthocarbonate (II).

Biemann (3) noted that *O*-isopropylidene derivatives are most suitable for the determination of the molecular weight of carbohydrates because the loss of one of the methyl groups from the 2,2-dimethyl-1,3-dioxolane ring gives rise to an abundant fragment of mass M — 15. Indeed, the spectrum of II shows a strong peak at 517. Other peaks in the spectrum were interpreted as follows: 502 (M — 2CH_3), 474 (M — $(CH_3)_2C{=}O$), 459 (474 — CH_3), 444 (459 — CH_3), 431 (M — ), 289 ( +H), 101 (), 59 (($(CH_3)_2C{=}O$ + H)), and 43 (C_2H_3O). Several of these fragments were shown by DeJongh and Biemann (3) to be characteristic of O-isopropylidene sugars.

Mass peaks at 193, 222, and 251 each had what appeared to be isotope peaks at 1/2 mass unit higher. These isotope peaks indicate that the 193, 222, and 251 fragments are doubly charged ions of masses 386, 444, and 502, respectively. The 386, 444, and 502 ions are all formed by double dissociations, and no doubly charged ions are found for the large 517 peak or other ions formed by a single dissociation. It would thus appear that doubly ionized molecules form double dissociated ions.

Whereas II was stable under strongly alkaline conditions, on mild acid hydrolysis II formed D-mannitol and a carbonyl-containing compound presumed to be D-mannitol 1,4-carbonate. When the hydrolysis was stopped after a short time, 2,3:5,6-di-O-isopropylidene-D-mannitol was detected.

Although the precise mechanism for the formation of II cannot be formulated at present, a thionocarbonate derivative is assumed to be formed as an intermediate, since the reaction of 2,3:5,6-di-O-isopropylidene-D-mannitol with thiophosgene also gave II.



I II

References

1. W. M. Doane, B. S. Shasha, C. R. Russell, and C. E. Rist, *J. Org. Chem.* **30**, 162 (1965).
2. The mass spectrum was measured on a Nuclide 12-90-G mass spectrometer equipped with a probe inlet and operated at a crucible temperature of 180°. This instrument is named merely as part of the exact experimental conditions. Naming it does not constitute an endorsement of this product over those of other manufacturers.
3. Don C. DeJongh and K. Biemann, *J. Am. Chem. Soc.* **86**, 67 (1964).