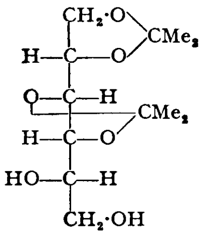
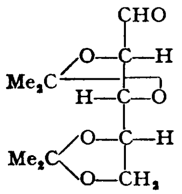
596. *The* 2 : 3-4 : 5-*Di*iso*propylidene Derivatives of* aldehydo-L-*Xylose and* L-*Xylitol.*

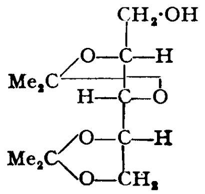
By E. J. Bourne, G. P. McSweeney, and L. F. Wiggins.

2 : 3-4 : 5-Di*iso*propylidene *aldehydo*-L-xylose, prepared from 1 : 2-3 : 4-di*iso*propylidene L-iditol by oxidation with periodate, has been characterised and some of its crystalline derivatives are described. It has been converted into 2 : 3-4 : 5-di*iso*propylidene L-xylitol by hydrogenation.

In a previous paper (Bourne, McSweeney, and Wiggins, *J.*, 1952, 2542), part of the evidence presented in support of the conclusion that di*iso*propylidene L-iditol (I) carries the acetone residues in the 1 : 2- and 3 : 4-positions was that the compound consumed 1 mol. of periodate with the concomitant production of formaldehyde, and it was noted that the major product of the oxidation should have been 2 : 3-4 : 5-di*iso*propylidene *aldehydo*-L-xylose (II), a compound which has been obtained hitherto only in admixture with 2 : 3-4 : 5-di*iso*propylidene *aldehydo*-D-arabinose (Bourne, McSweeney, Stacey, and Wiggins, *J.*, 1952, 1408). We have now repeated the oxidation on a larger scale and have, in fact, isolated a syrup, analysis of which was correct for a di*iso*propylidene pentose. As confirmation that the pentose moiety was L-xylose, the sugar produced on hydrolysis of this syrup yielded the known β-tetra-acetyl L-xylose with acetic anhydride–sodium acetate, and, when submitted to filter-paper chromatography, gave one spot, having an R_F value identical with that of an authentic specimen of xylose, used as a standard on the same chromatogram.


(I)


(II)


(III)

2 : 3-4 : 5-Di*iso*propylidene *aldehydo*-L-xylose exhibited the usual aldehydic properties inasmuch as it gave a semicarbazone, an oxime, and a bisdimedone derivative, all crystalline. The bisdimedone compound, like that of the isomeric 2 : 3-4 : 5-di*iso*propylidene *aldehydo*-D-arabinose (*loc. cit.*), was insoluble in water, a fact which explained why, in our previous work (*J.*, 1952, 2542), the formaldehyde liberated during periodate oxidation of 1 : 2-3 : 4-di*iso*propylidene L-iditol could be characterised as its water-insoluble dimedone derivative only after it had been purified by distillation in steam.

Hydrogenation of 2 : 3-4 : 5-di*iso*propylidene *aldehydo*-L-xylose in ethyl alcohol in the presence of Adams's platinum oxide afforded a syrupy non-reducing di*iso*propylidene pentitol, which gave a crystalline toluene-*p*-sulphonate. In view of the route by which it had been prepared, there can be little doubt that this syrup was 2 : 3-4 : 5-di*iso*propylidene L-xylitol (III, synonymous with 1 : 2-3 : 4-di*iso*propylidene D-xylitol); it was probably the L-isomer of 2 : 3-4 : 5-di*iso*propylidene DL-xylitol which results from the treatment of xylitol with acetone, anhydrous copper sulphate, and concentrated sulphuric acid (cf.

Tipson and Cretcher, *J. Org. Chem.*, 1943, **8**, 95; Hann, Ness, and Hudson, *J. Amer. Chem. Soc.*, 1944, **66**, 73).

EXPERIMENTAL

1 : 2-3 : 4-5 : 6-Tri*iso*propylidene L-iditol, prepared as described by Bourne, McSweeney, and Wiggins (*loc. cit.*), had m. p. 57—58° alone or on admixture with an authentic specimen, $[\alpha]_D^{16}$ $+5{\cdot}8°$ (*c*, 5·5 in chloroform) (Found : C, 59·5; H, 8·6. Calc. for $C_{15}H_{26}O_6$: C, 59·6; H, 8·7%).

1 : 2-3 : 4-Di*iso*propylidene L-iditol (*loc. cit.*) had b. p. 136—140° (bath-temp.)/0·005 mm., $[\alpha]_D^{19}$ $+23{\cdot}8°$ (*c*, 2·9 in ethyl alcohol) (Found : C, 54·8; H, 8·5. Calc. for $C_{12}H_{22}O_6$: C, 54·9; H, 8·5%).

2 : 3-4 : 5-*Di*iso*propylidene* aldehydo-L-*Xylose*.—To an aqueous solution (20 c.c.) of 1 : 2-3 : 4-di*iso*propylidene L-iditol (6·50 g.) a solution (20 c.c.) of sodium metaperiodate (6·60 g.) was added slowly at 0°. After 24 hours, the solution was saturated with sodium chloride and extracted exhaustively with chloroform. The extracts were dried ($MgSO_4$), filtered, and evaporated at 40° to a syrup (5·0 g.), which was fractionally distilled. The main fraction, 2 : 3-4 : 5-*di*iso*propylidene* aldehydo-L-*xylose*, was a colourless mobile syrup (3·24 g.), b. p. 92—100° (bath-temp.)/0·04 mm., n_D^{16} 1·4545, $[\alpha]_D^{19}$ $+25{\cdot}6°$ (*c*. 3·2 in ethyl alcohol), $[\alpha]_D^{18}$ $+25{\cdot}2°$ (*c*, 3·9 in methyl alcohol) (Found : C, 57·0; H, 8·0. $C_{11}H_{18}O_5$ requires C, 57·4; H, 7·9%). The syrup became viscous when kept at room temperature for a day. The *semicarbazone* had m. p. 175—176°, $[\alpha]_D^{18}$ $+29{\cdot}4°$ (*c*, 2·7 in chloroform) (Found : C, 50·3; H, 7·6; N, 14·3. $C_{12}H_{21}O_5N_3$ requires C, 50·2; H, 7·4; N, 14·6%). The *oxime* had m. p. 90—91°, $[\alpha]_D^{19}$ $+19{\cdot}1°$ (*c*, 2·5 in ethyl alcohol) (Found: C, 53·7; H, 7·8; N, 5·7. $C_{11}H_{19}O_5N$ requires C, 53·9; H, 7·8; N, 5·7%). The *bisdimedone* derivative had m. p. 111—112°, $[\alpha]_D^{16}$ $-26{\cdot}6°$ (*c*, 3·8 in chloroform) (Found: C, 65·9; H, 8·3. $C_{27}H_{40}O_8$ requires C, 65·8; H, 8·2%).

Hydrolysis of 2 : 3-4 : 5-*Di*iso*propylidene* aldehydo-L-*Xylose*.—The xylose derivative (1·00 g.) was treated with N-sulphuric acid at 100° for 3 hours; the solution was neutralised with barium carbonate and filtered, the filtrate being evaporated to a syrup (0·60 g.). Paper-chromatographic analysis of a portion of the syrup, with the upper phase of a mixture of butanol (40%), ethanol (10%), ammonia (1%), and water (49%) as the solvent, and a butanol solution of aniline hydrogen phthalate as the spray (cf. Partridge, *Nature*, 1949, **164**, 443), revealed one component; this had an R_F value identical with that of xylose, used as a standard on the same chromatogram.

The remainder of the syrup was treated with acetic anhydride (3 c.c.) and fused sodium acetate (0·8 g.) at 100° for 1 hour. The precipitate obtained when the reaction mixture was poured into water was recrystallised from aqueous ethyl alcohol, to give tetra-acetyl β-L-xylose (0·40 g.), m. p. and mixed m. p. 125°, $[\alpha]_D^{22}$ $+25{\cdot}8°$ (*c*, 2·0 in chloroform). Appel (*J.*, 1935, 425) gave m. p. 127—128·5°, $[\alpha]_D^{15}$ $+25{\cdot}7°$ (in chloroform) for this compound; Vargha (*Ber.*, 1935, **68**, 18) recorded m. p. 126°, $[\alpha]_D^{20}$ $+25{\cdot}7°$ (in chloroform).

2 : 3-4 : 5-*Di*iso*propylidene* L-*Xylitol*.—A solution of 2 : 3-4 : 5-di*iso*propylidene *aldehydo*-L-xylose (2·00 g.) in ethyl alcohol (20 c.c.) was shaken with Adams's platinum oxide catalyst (0·07 g.) in the presence of hydrogen under slight pressure until absorption ceased. The mixture was filtered and the filtrate was evaporated at 12 mm. to a syrup, which was then fractionally distilled. The main fraction, 2 : 3-4 : 5-*di*iso*propylidene* L-*xylitol* (1·60 g.), had b. p. 96—98° (bath-temp.)/0·03 mm., n_D^{21} 1·4570, $[\alpha]_D^{18}$ $+12{\cdot}5°$ (*c*, 3·6 in ethyl alcohol) (Found : C, 56·8; H, 8·8. $C_{11}H_{20}O_5$ requires C, 56·9; H, 8·7%). 2 : 3-4 : 5-Di*iso*propylidene DL-xylitol, prepared directly from xylitol and acetone, has m. p. 33—34·5° (Tipson and Cretcher, *loc. cit.*; Hann, Ness, and Hudson, *loc. cit.*), and can be crystallised only with difficulty in the absence of seed crystals.

2 : 3-4 : 5-*Di*iso*propylidene* 1-*toluene*-p-*sulphonyl* L-*xylitol*, prepared by toluene-*p*-sulphonyl chloride in dry pyridine at 25° (20 hours), crystallised from aqueous ethyl alcohol as needles, m. p. 65—66°, $[\alpha]_D^{20}$ $+16{\cdot}3°$ (*c*, 4·4 in ethyl alcohol) (Found : C, 56·0; H, 6·8; S, 8·1. $C_{18}H_{26}O_7S$ requires C, 55·9; H, 6·8; S, 8·3%). Like 2 : 3-4 : 5-di*iso*propylidene 1-toluene-*p*-sulphonyl DL-xylitol, the L-isomer decomposed spontaneously in a few days at room temperature. Recorded values of the m. p. of the DL-isomer are 70—71° (Tipson and Cretcher, *loc. cit.*) and 77—78° (Hann, Ness, and Hudson, *loc. cit.*).

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