smeared out), the configuration being about midway between eclipsed and staggered, as in biferrocenyl (3). As a result of the disorder, the further refinement required to establish the structure and configuration more precisely is not profitable; we hope to obtain more accurate information from a study of diferrocenyl ketone. The fact that the rings bonded to the iron atom do have the same disposition as those bonded to the ruthenium suggests that the configuration is influenced to a great extent by intermolecular interactions. The central rings are not quite coplanar, each being rotated a few degrees out of the $C_1C_1'C_{11}O$ plane. No accurate molecular dimensions are available from this study, but all the intra- and inter-molecular distances appear to be normal.

ACKNOWLEDGMENTS

The authors are indebted to the National Council of Canada for financial support, to Dr. M. D. Rausch for the crystal sample, to Dr. F. R. Ahmed for kindly making available his I.B.M. 1620 programs, and to the staff of the U.B.C. Computing Centre for assistance.

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RECEIVED MARCH 2, 1964.
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## HYDROGENOLYSIS OF CARBOHYDRATES. X. HYDROGENOLYSIS OF (±)-EPI-INOSOSE-2[1,2]

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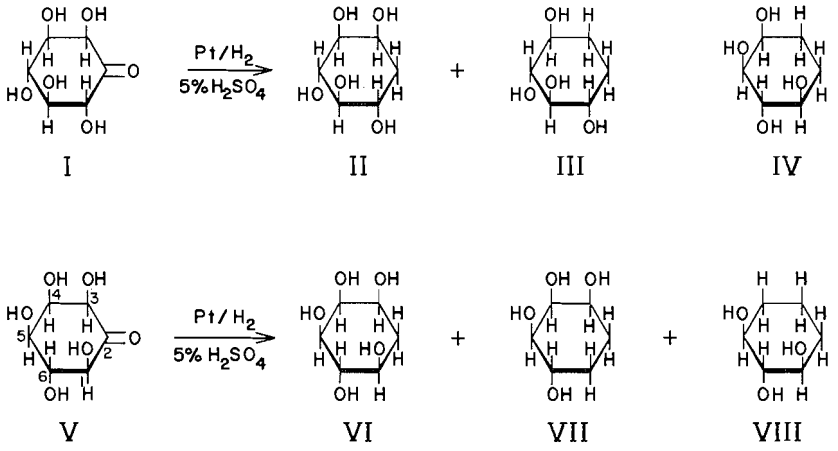
Posternak has shown that catalytic hydrogenation of scyllo-inosose using a platinum catalyst in 5% aqueous sulphuric acid results in the formation of scyllo-quercitol (1). More recently Post and Anderson found that hydrogenation of (+)-vibo-inosose (I) under similar conditions yields (+)-vibo-quercitol (II) and 1,3/2,4-cyclohexanetetrol (III), that is, the tetrol is formed from the inosose by reductive removal of the keto and its adjacent hydroxyl group. This reaction is general among substituted inososes having an axial hydroxyl vicinal to the keto group (2).

In the present work it was observed that by-products were formed during the preparation of (±)-epi-quercitol (VI) from (±)-epi-inosose-2 (V) (purified via its phenylhydrazone (3)). Fractionation of the product on a cellulose column gave tetrol and triol fractions as well as (±)-epi-quercitol. The former consisted mainly of (±)-1,2,3/4-cyclohexanetetrol (VII), which was identified, subsequent to measurement of its periodate characteristics, by comparison with an authentic specimen (4). Oxidation of the triol fraction with sodium periodate resulted in consumption of 2.0 moles of oxidant with concomitant production of 0.9 moles of acid. After crystallization the triol had a melting point corresponding to 1,3/2-cyclohexanetriol (5) (VIII) and differing from those of the 1,2,3- (6) and 1,2/3-isomers (5). Although an authentic specimen was not available the identification was

[1]*Carried out, in part, through the courtesy of Prof. S. J. Angyal, University of New South Wales, Sydney, Australia.*
[2]*Issued as N.R.C. No. 7953.*




confirmed by examination of the nuclear magnetic resonance (n.m.r.) spectrum of the derived triacetate. It gave one acetoxy-proton signal in the n.m.r. at 2.0 p.p.m., thus indicating three equatorial acetoxy groups. In polyacetoxycyclohexanes which do not interconvert readily from one chair form to the other, equatorial acetoxy protons give signals at 2.0–2.1 p.p.m. Axial acetoxy protons produce signals at slightly lower field. This relation of chemical shift to conformation has been demonstrated with myo-, levo- (7), epi-, and neo-inositol hexaacetates (8) and the acetates of stereoisomeric quinic acid and quinicol derivatives (9).

The mixture, formed by hydrogenolysis of (±)-epi-inosose-2, was acetylated and examined by gas phase chromatography. On a molar basis the composition of the acetate mixture was as follows: (±)-epi-inositol (7%), (±)-epi-quercitol (53%), (±)-1,2,3/4-cyclohexanetetrol (21%), 1,3/2-cyclohexanetriol (9%). Smaller amounts of an unidentified tetrol acetate (5%) and two triol acetates (1% each) were detected. The (±)-1,2,4/3-cyclohexanetetrol tetraacetate was shown to be absent from the mixture.

In the light of the results obtained by Posternak (1) and Post and Anderson (2) it was not anticipated that hydrogenation of (±)-epi-inosose-2 would give appreciable amounts of tetrols and triols. Reductive elimination of the equatorial hydroxyl at C-1 and the keto group takes place, to yield (±)-1,2,3/4-cyclohexanetetrol (VII). A similar elimination at C-3 to form (±)-1,2,4/3-cyclohexanetetrol (IV) does not occur. Instead it appears that the platinum–cyclitol intermediate involving C-2 and C-3 is further hydrogenolyzed at C-4 to give 1,3/2-cyclohexanetriol. In this case the C-4 substituents have a reactivity comparable to those containing an axial hydroxyl group vicinal to a keto group in inososes.

## EXPERIMENTAL

The (±)-epi-inosose-2 was prepared by the method of Posternak (10). A crude sample had C, 39.30; H, 5.84. Calc. for $C_6H_{10}O_6$: C, 40.45; H, 5.66%. After purification via its phenylhydrazone and two recrystallizations from water a sample had C, 39.92; H, 5.79%. Examination of the phenylhydrazone and semicarbazone (3) reaction mixtures on a paper chromatogram (solvent: *n*-butanol–ethanol–water 40:11:19 v/v; spray: ammoniacal silver nitrate) did not indicate the presence of any disubstituted derivatives. Melting points are corrected to the nearest degree.

*Hydrogenation of* (±)-*epi-Inosose-2*

The (±)-epi-inosose-2 (2.0 g) was suspended in 5% sulphuric acid (50 ml) and shaken overnight with platinic oxide (0.20 g) in the presence of hydrogen. The solution was filtered, neutralized with barium carbonate, filtered, and evaporated. The product gave on a paper chromatogram (solvent and spray as above)

a main spot corresponding to epi-quercitol, and two others running at a faster rate. A trace of epi-inositol was present also.

The product was acetylated and examined by gas phase chromatography using 2% LAC IR296 on Chromosorb W as column packing (11). The gas–liquid chromatograph unit was of conventional design using thermal conductivity cells for detection. At 200 °C a satisfactory separation of epi-inositol, epi-quercitol, and tetrol acetates was obtained and at 160 °C the triol, tetrol, and epi-quercitol acetates gave suitable signals.

The responses of the machine were calibrated using authentic cyclitol acetates. On a molar basis the product consisted of the acetates of (±)-epi-inosose (7%), (±)-epi-quercitol (53%), (±)-1,2,3/4-cyclohexanetetrol (21%), 1,3/2-cyclohexanetriol (9%). An unidentified tetrol acetate (5%), with a slightly higher retention time than the main tetrol acetate, and two triol acetates (1% each), which had higher and lower retention times than the main triol acetate, respectively, were also detected.

The acetate of (±)-1,2,4/3-cyclohexanetetrol (4) was shown to have a lower retention time than the (±)-1,2,3/4-isomer (4).

*Isolation of Hydrogenolysis Products*

The above hydrogenolysis product was fractionated on a cellulose column using *n*-butanol one-half saturated with water as eluant. The following materials were isolated:

(i) *Triol*—140 mg was isolated and oxidation of this material with aqueous sodium periodate resulted in the consumption of 1.97 moles of oxidant in one day with concomitant production of 0.94 moles of acid.

One crystallization from ethyl acetate yielded 104 mg of material and a further recrystallization from the same solvent gave 1,3/2-cyclohexanetriol with m.p. 107–108 °C. Calc. for $C_6H_{12}O_3$: C, 54.5; H, 9.15. Found: C, 54.6; H, 9.4%. McRae *et al.* (5) report m.p. 107.7–108.2 °C for the 1,3/2-isomer, whereas the 1,2,3-isomer has m.p. 145 °C (6) and the 1,2/3-isomer m.p. 125 °C (5). After 5 h the triol consumed 1.97 moles of sodium periodate releasing 1.05 moles of acid.

The triacetate, obtained by the hot sodium acetate – acetic acid anhydride method, was recrystallized twice from hexane to give a product with m.p. 128–129 °C. Calc. for $C_{12}H_{18}O_6$: C, 55.8; H, 7.0. Found: C, 55.6; H, 7.0%. In the n.m.r., using chloroform as solvent, it gave one signal for acetoxy protons at 2.00 p.p.m. (tetramethyl silane standard).

(ii) *Tetrol*—324 mg was isolated from the column and this was recrystallized from ethanol. The product (0.23 g) was recrystallized and had m.p. 158–159 °C. Calc. for $C_6H_{12}O_4$: C, 48.6; H, 8.2. Found: C, 48.75; H, 8.2%. After 5 and 24 h the tetrol consumed 3.0 moles of sodium periodate, yielding 2.0 moles of acid. The tetrol gave an X-ray diffraction pattern identical with (±)-1,2,3/4-cyclohexanetetrol (4). The derived tetraacetate was recrystallized twice from ether–hexane and had m.p. 113–114 °C. Calc. for $C_{14}H_{20}O_8$: C, 53.3; H, 6.4. Found: C, 53.0; H, 6.45%.

(iii) (±)-*epi-Quercitol*—The majority of the product was represented by epi-quercitol (1.05 g) with m.p. 187–190 °C after two recrystallizations from aqueous ethanol. Calc. for $C_6H_{12}O_5$: C, 43.9; H, 7.4. Found: C, 43.9; H, 7.35%.

## ACKNOWLEDGMENTS

The author thanks Prof. T. Posternak for the gift of (±)-1,2,3/4- and (±)-1,2,4/3-cyclohexanetetrols. Thanks are also due to Dr. E. Challen of the University of New South Wales and Mr. M. Mazurek for carrying out carbon and hydrogen analyses, and Mr. W. C. Haid for an n.m.r. determination.

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Received November 8, 1964.
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