

EXPERIMENTS IN THE FURAN SERIES. XVI.*

HYDROXYLATION OF THE PRODUCTS OF METHOXYLATION OF FURAN DERIVATIVES SUBSTITUTED IN THE POSITION 3

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3-Acetylfuran (*I*), 3-(1-hydroxyethyl)furan (*II*) and 3-(1-acetoxyethyl)furan (*III*) were submitted to electrolytic methoxylation. In the case of products *IV*, *V* and *VI* *cis*-hydroxylation of the 3,4-double bond was followed.

In our previous paper we investigated the synthetic exploitation of additions to the double bond of cyclic five-membered acetals formed on alkoxylation of furan compounds¹⁻⁷. From the point of view of the synthesis of racemic sugars with branched carbon atom chain furan derivatives substituted in the position 3 must be used as starting material. The carbon atom chain of streptose⁸ corresponds to the structure of 3-acetylfuran (*I*), 3-(1-hydroxyethyl)furan (*II*) and 3-(1-acetoxyethyl)furan (*III*). Therefore electrolytic methoxylation of these compounds and *cis*-hydroxylation of the products was investigated as a way to prepare configuration isomers of the mentioned sugar.

All described routes used for the preparation of compounds *I-III* have been evaluated, but simultaneously new methods of their preparation also had to be tried. Among new syntheses of 3-acetylfuran (*I*) ketone-forming cleavage of the described ethyl 3-furoylacetate⁹ was tried. The cleavage proper takes place in good yield (90.5%). The weak point of the synthesis is Claisen condensation which we were able to reproduce only in a 49% yield. Another novel synthesis of ketone *I* was carried out on reaction of 3-furoyl chloride with dimethylcadmium. While the starting chloride could be prepared from the acid in an 82% yield the reaction proper takes place only in a 33% yield. We consider that the preparation of ketone *I* by Grignard synthesis from 3-cyanofuran, worked out in our laboratory, is optimum¹⁰. Alcohol *II* is formed on reaction of methylmagnesium iodide with 3-formylfuran in 69% yield, on reduction of ketone *I* with lithium aluminum hydride in a 52% yield. The most efficient synthesis of this compound seems to us, however, to be its preparation

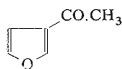
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from 3-bromofuran¹⁰ via 3-furyllithium. When acetaldehyde is treated with organolithium reagent at -70°C alcohol *II* is formed in a 56% yield. Acetylation of alcohol *II* to 3-(1-acetoxyethyl)furan *III* was carried out with acetic anhydride in pyridine.

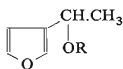
Electrolytic methoxylation of ketone *I* takes place without the formation of by-products only at temperatures below -50°C , when 3-(1,1-dimethoxyethyl)-2,5-dimethoxy-2,5-dihydrofuran (*IV*) is formed in 21.5% yield as the sole product. The formation of ketal in this reaction is not an isolated phenomenon and it was also observed during the electrolytic methoxylation of 2-acetylfuran^{11,12}. The methyl group in the side chain of compound *IV* gives in the PMR spectrum a doublet which may be explained on the basis of a high conformational barrier. This assumption was made on the basis of a study on models. Unless a low temperature was maintained during the methoxylation the reaction gives a higher yield but a solid substance appeared in the product which according to its elemental analysis corresponds to 3-acetyl-dimethoxy-2,5-dihydrofuran. This substance, however, melts within a broad temperature interval, and an analysis of the PMR spectrum indicates the presence of two substances which we were unable to separate. In order to prevent the formation of a large amount of hydrolytic products the electrolytic methoxylation of 3-(1-hydroxyethyl)furan (*II*) also has to be carried out at temperature below -50°C (ref.¹³). During the reaction 3-(1-hydroxyethyl)-2,5-dimethoxy-2,5-dihydrofuran (*V*) is formed. This compound must be freed from all traces of acids before distillation if polymerization is to be avoided. Gas chromatographic analysis of the products proved that it contained 86% of one of the isomers of compound *V*, having both methoxy groups in *cis*-configuration, as followed from the results of hydroxylation. In these case of the compound *II* IR spectroscopy demonstrated intermolecular hydrogen bonds indicating the association of two molecules of this compound. This association makes the access of the methoxy groups from one side easier, and it favours *cis*-methoxylation. For the synthesis of *ribo*- and *lyxo*-isomers of streptose from compound *V* two routes come into consideration: Either *trans*-hydroxylation of the double bond of this compound⁵, or the cleavage of the ring, catalysed with hydrogen chloride^{14,15}. Both routes are unrealistic in view of the fact that large amounts of resins are formed in both cases. *cis*-Hydroxylation leads to *arabo*- and *xylo*-isomers. Electrolytic methoxylation of the acetate *III* takes place without complications and the 3-(1-acetoxyethyl)-2,5-dimethoxy-2,5-dihydrofuran (*VI*) formed is a stable compound.

The only suitable method of *cis*-hydroxylation of acetals *IV*–*VI* was found to be oxidation with permanganate in the presence of magnesium sulfate at low temperatures in water-miscible solvents^{1,16,17}, of which aqueous acetone seems best. Isolation yield is favourably influenced if the separated manganese dioxide is decomposed with sulfur dioxide. Oxidation with osmium tetroxide is not suitable because partial hydrolysis of the acetal bonds takes place. Hydroxylation products are unstable during distillation and therefore, unless crystalline, they were purified *via* the stable

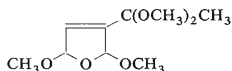
acetyl derivatives VII–IX. From these pure diols were obtained on treatment with sodium methoxide solution¹⁸.



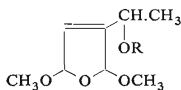
I



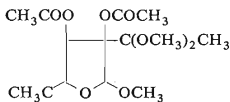
II, R = H
III, R = COCH₃



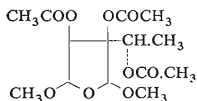
IV



V, R = H
VI, R = COCH₃



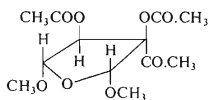
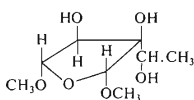
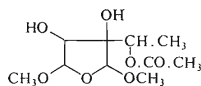
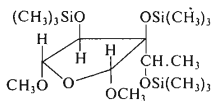
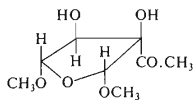
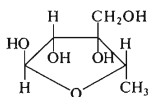
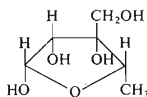
VII



VIII

On hydroxylation of acetal IV and subsequent acetylation of the product 3-(1,1-dimethoxyethyl)-2,5-dimethoxy-3,4-diacetyltetrahydrofuran (VII) was obtained. From the products of *cis*-hydroxylation of alcohol V substance X crystallised out which was identified as 3-(1-hydroxyethyl)-2,5-dimethoxy-3,4-dihydroxytetrahydrofuran; relative configurations on all its four carbon atoms was established. On the basis of the Overhauser effect PMR spectroscopy proved mutual *cis*-position of the methoxy group in the position 2 to the side chain. Irradiating the side chain methyl protons (with frequency of 108.9 Hz) the intensity of the methoxy protons (3.36 δ) increased by 34%, while the intensities of other signals remained unchanged. Therefore the idea must be considered that the methoxyl group in the position 2 is sterically close to the side chain. As the mutual *cis*-configuration of the hydroxy groups is given by the synthesis, only the configuration of the hydrogen in the position 5 remains to be elucidated. As the coupling constant $J_{4,5}$ of the compound X is equal to 3.7 Hz the hydrogens in 4 and 5 have evidently *trans*-configuration, similarly as in the case of the isomer of the related dihydroxystreptose XIVa for which the NMR spectrum of both anomers has been described⁸. The crystalline isomer X was transformed to tris-trimethylsilyl derivative XII so that it might be

used as standard for the explanation of the composition of the reaction mixture from which it was isolated. This mixture was submitted to the same operation and the mixture of isomeric tris-trimethylsilyl derivatives was investigated by the method of gas chromatography, combined with mass spectrometry. It was shown that this mixture contained 5 products of which 3 have the same mass spectrum as the standard substance *XII*, and, therefore, they must be its isomers. After acetylation of the crude mixture of trihydroxy derivatives and after distillation a substance crystallised out the composition of which corresponds to 3-acetyl-2,5-dimethoxy-3,4-diacetoxy-tetrahydrofuran (*IX*). During *cis*-hydroxylation of alcohol *V* a partial oxidation of the secondary alcohol group evidently takes place. This compound has on all carbon atoms a similar configuration as the crystalline triol *X*. On the basis of the Overhauser effect the mutual *cis*-position of the acetyl group and the methoxy group in the position 2 was proved. When the spectrum was measured with an additional frequency of 181.5 Hz the intensity of the proton signals of the methoxyl groups in the position 2 ($\delta = 3.39$) increased by 30%. The position of the acetoxy groups is given by synthesis. The coupling constant $J_{4,5} = 3$ Hz corresponds to the *trans*-configuration of both hydrogens, according to the comparison of the coupling constants of both anomers of dihydrostreptose (*XIVa*, $J_{4,5} = 3,7$ Hz, *XIVb*, $J_{4,5} = 5.1$ Hz). From this it follows that the mutual position of the methoxyl groups is *cis*. Under the effect of sodium methoxide on diacetyl derivative *IX* 3-acetyl-2,5-dimethoxy-3,4-dihydroxytetrahydrofuran (*XIII*) was formed.

*IX**X*, $J_{4,5} = 3.7$ Hz*XI**XII**XIII**XIVa*, $J_{4,5} = 3.8$ Hz*XIVb*, $J_{4,5} = 5.1$ Hz

Hydroxylation of acetate *VI* takes place without complications and the relatively stable 3-(1-acetoxyethyl)-2,5-dimethoxy-3,4-dihydroxytetrahydrofuran (*XI*) is formed. It was acetylated to 3-(1-acetoxyethyl)-2,5-dimethoxy-3,4-diacetoxytetrahydrofuran (*VIII*) and the latter gave on reaction with sodium methoxide a mixture of configurational isomers of the triol with which it has identical analysis and infrared spectrum.

A series of further experiments demonstrated that the compounds *VII*, *X* and *XI* are unsuitable for further synthetic plans. With these compounds a cleavage of the tetrahydrofuran ring takes place only under conditions when the reaction products polymerize quantitatively.

EXPERIMENTAL

The temperature data are not corrected. The substances were dried before analysis *in vacuo* (1 Torr) at room temperature for 12 hours. The PMR spectra were measured on the following apparatuses: HX-90, Bruker Physik AG Karlsruhe et Spectrospin AG Zürich, 90 MHz; JEOL JNM-3-60, 60 MHz; Tesla BS 487 A, 80 MHz and BS 477, 60 Hz. The infrared spectra were measured on UR-10, Carl Zeiss, Jena, and Perkin-Elmer 325. The mass spectra were taken on Gas Chromatograph-Mass Spectrometer LKB-9000. For gas chromatography on this apparatus a 2 m column with SE-30 packing was used. Gas chromatography was carried out on a Carlo Erba Fractovap Model D apparatus with a 2.5 m column with Carbowax 20M, and on Chrom-2 apparatus.

3-Acetylfuran (*I*)

A) A mixture of 21 g (0.12 mol) of ethyl 3-furoylacetate⁹ and 300 ml of 5% hydrochloric acid was heated on a water bath for 4 hours. After cooling the mixture was extracted with ether, the extract washed with sodium hydrogen carbonate and water, and dried over anhydrous magnesium sulfate. Ether was distilled off and the residue crystallised from light petroleum to yield 11.5 g (90.5%) of ketone *I*, m.p. 54°C (lit.^{19,20} gives m.p. 53–54°C).

B) To a solution of Grignard reagent prepared from 1.9 g of magnesium (0.08 mol) and 10.7 g (0.08 mol) of methyl iodide 7.1 g of cadmium chloride were added in portions at 0°C and the mixture was refluxed for 20 minutes. Benzene (40 ml) was added to the mixture twice under simultaneous distilling off of the same volume of distillate. After cooling a solution of 8 g (0.05 mol) of 3-furoyl chloride in 20 ml benzene was added to it and the mixture refluxed for one hour and decomposed with dilute sulfuric acid. The product was extracted with ether and the extract washed with potassium carbonate solution and water, and dried over magnesium sulfate. Ether was evaporated and ketone *I*, m.p. 54°C, crystallised from light petroleum, yield 2.5 g (30%).

3-(1-Hydroxyethyl)furan (*II*)

A) To a solution of Grignard reagent prepared from 6.1 g (0.25 mol) of magnesium and 42.8 g (0.3 mol) of methyl iodide in 300 ml of ether a solution of 20 g (0.21 mol) of 3-formylfuran in 200 ml of ether was added dropwise. Under stirring the mixture was refluxed for 2 hours and after cooling it was decomposed with a saturated ammonium chloride solution. The ethereal layer was washed with water and dried over anhydrous magnesium sulfate. After evaporation of ether the residue was distilled to give 5 g (69%) of alcohol *II*, b.p. 75°C/15 Torr. For C₆H₈O₂ (112.1) calculated: 64.28% C, 7.19% H; found: 64.26% C, 6.97% H. IR spectrum: 883, 970, 1039, 1078, 1168, 1240, 1328, 1381, 1456, 1506, 2871, 2921, 3370 and 3615 cm⁻¹.

B) To a solution of 1.8 mol of butyllithium in ether, kept under nitrogen, 220 g (0.68 mol) of 3-bromofuran in 700 ml of ether were added under stirring at -70°C , and after 15 minutes stirring a solution of 132 g (3.14 mol) of acetaldehyde in 500 ml of ether was added dropwise to it. After an additional 2 hours of stirring in the cold the mixture was allowed to stand for 24 hours at room temperature and then decomposed with a saturated ammonium chloride solution. After evaporation of ether distillation of the residue gave 109 g (56% of alcohol II).

C) A solution of 55 g (0.5 mol) of 3-acetylfuran (I) in 300 ml of ether was added dropwise to a suspension of 10 g (0.26 mol) of lithium aluminium hydride in 300 ml of ether at such a rate as would keep the mixture mildly boiling. Heating was continued for another hour. After cooling the mixture was decomposed with 5% sulfuric acid. The ethereal extract was washed with a potassium carbonate solution and water, and dried over magnesium sulfate. After evaporation of ether vacuum distillation of the residue gave 30 g (52%) of alcohol II.

3-(1-Acetoxyethyl)furan (III)

To a solution of 80 g of alcohol II in 900 ml of pyridine 225 ml of acetic anhydride were added at 0°C and the mixture allowed to stand at room temperature for 48 hours. It was then poured on 1.5 kg of ice and extracted with ether. The ethereal layer was dried over anhydrous magnesium sulfate. First ether was distilled off and then pyridine in a vacuum. Further distillation gave 84 g (76%) of acetate III, b.p. $84^{\circ}\text{C}/12$ Torr. For $\text{C}_8\text{H}_{10}\text{O}_3$ (154.2) calculated: 62.35% C, 6.55% H; found: 62.30% C, 6.58% H.

Electrolytic Methoxylation (general method)

Electrolytic methoxylations were carried out in 300 ml of methanolic solution (volume of the electrolyser) in the presence of 6 g of ammonium bromide as electrolyte. The reaction took place on a graphite anode at 25 V and 4–4.5 A, at low temperatures. After the reaction, the end of which is indicated by the increase in resistance, the reaction mixture was neutralised with a solution of sodium methylate to pH 8. Methanol was evaporated *in vacuo* and the remaining product dissolved in ether and dried over sodium sulfate. The products were purified by vacuum distillation.

3-(1,1-Dimethoxyethyl)-2,5-dimethoxy-2,5-dihydrofuran (IV) was obtained from 24 g (0.22 mol) of ketone I (25 A. h) at -55°C in a 10.2 g (21.4%) yield, b.p. $68^{\circ}\text{C}/0.7$ Torr. For $\text{C}_{10}\text{H}_{18}\text{O}_5$ (218.3) calculated: 55.03% C, 8.31% H, 45.17% OCH_3 ; found: 55.24% C, 8.17% H, 45.03% OCH_3 . Infrared spectrum: 912, 961, 978, 1030, 1086, 1101, 1137, 1211, 1256, 1300, 1351, 1376, 1480, 1561, 2831, 2906, 2932, 3001 cm^{-1} . PMR spectrum: 1.38 (3 H, d, CH_3), 3.23 (12 H, m, OCH_3) and 5.50 (3 H, m, nucleus) δ .

Bis-dinitrophenylhydrazone: crystallised from nitromethane, it melts under decomposition. For $\text{C}_{20}\text{H}_{22}\text{N}_8\text{O}_{10}$ (564.5) calculated: 44.95% C, 4.15% H, 20.98% N; found: 44.87% C, 3.99% H, 19.98% N.

3-(1-Hydroxyethyl)-2,5-dimethoxy-2,5-dihydrofuran (V) was prepared from 40.5 g of alcohol II (50 A. h) at -50°C , in a 83.8% yield (43.5 g), b.p. $91^{\circ}\text{C}/0.4$ Torr. For $\text{C}_8\text{H}_{14}\text{O}_4$ (174.2) calculated: 55.18% C, 7.92% H, 35.63% OCH_3 ; found: 55.19% C, 7.95% H, 35.49% OCH_3 . IR-spectrum: 884, 940, 972, 1021, 1090, 1195, 1310, 1380, 1454, 2828, 2921, 3470 and 3610 cm^{-1} .

3-(1-Acetoxyethyl)-2,5-dimethoxy-2,5-dihydrofuran (VI) was prepared from 15.4 g (0.1 mol) of acetate III at -35°C in 81% yield (17.5 g), b.p. $93^{\circ}\text{C}/0.3$ Torr. For $\text{C}_{10}\text{H}_{16}\text{O}_5$ (216.2) calculated: 55.55% C, 7.46% H, 28.84% OCH_3 ; found: 55.50% C, 7.47% H, 28.56% OCH_3 .

cis-Hydroxylation (general procedure)

To a solution of the unsaturated compound (0.4 mol) in 700 ml of acetone 1 600 ml of a solution containing 63.2 g (0.4 mol) of potassium permanganate and 58.8 g (0.4 mol) of magnesium sulfate heptahydrate were added under stirring at -15°C over 3 hours. Then the mixture was stirred for 2 hours and allowed to stand for 12 hours at room temperature. After cooling to 0°C sulfur dioxide was introduced into the mixture until manganese dioxide dissolved completely. The unreacted unsaturated starting compound was extracted with light petroleum and the aqueous solution was evaporated in a vacuum to a 1 200–1 500 ml volume and then saturated under cooling with potassium carbonate. The saturated solution was extracted continually with ether for 100 hours. The ethereal layer was dried over magnesium sulfate. After evaporation of ether the crude product was acetylated and the acetate distilled.

3-(1,1-Dimethoxyethyl)-2,5-dimethoxy-3,4-diacetyloxetetrahydrofuran (VII)

From 10 g (0.046 mol) of acetal IV 3.8 g (50.5%) of crude 3-(1,1-dimethoxyethyl)-2,5-dimethoxy-3,4-dihydroxytetrahydrofuran were obtained and 3.5 g of compound IV regenerated. The product was acetylated by the procedure described for the preparation of compound III, yielding 2.7 g (80%) of diacetate VII, b.p. $110^{\circ}\text{C}/0.2$ Torr. For $\text{C}_{14}\text{H}_{24}\text{O}_9$ (336.4) calculated: 49.99% C, 7.19% H, 30.42% OCH_3 ; found: 49.90% C, 7.01% H, 30.28% OCH_3 . IR spectrum: 896, 997, 1007, 1106, 1158, 1234, 1381, 1447, 1767, 2831, 2926, 2943 and 2997 cm^{-1} .

3-(1-Hydroxyethyl)-2,5-dimethoxy-3,4-dihydroxytetrahydrofuran (X)

From 17.4 g (0.1 mol) of alcohol V 8.1 g (47%) of a crude mixture of trihydroxy derivatives *Xa* was obtained. This product was dissolved in tetrachloromethane and pure compound *X* crystallised from the solution, m.p. $85-87^{\circ}\text{C}$, yield 12%. For $\text{C}_8\text{H}_{16}\text{O}_6$ (208.2) calculated: 46.15% C, 7.75% H, 29.81% OCH_3 ; found: 46.25% C, 7.74% H, 29.62% OCH_3 . Infrared spectrum: 890, 961, 989, 1070, 1106, 1176, 1201, 1378, 1456, 2831, 2926, 3001 and 3470 cm^{-1} . PMR spectrum: 1.17 ($J = 6.45$ Hz) (3 H, d, CH_3), 4.06 (1 H, q, CH in the side chain), 3.36 and 3.48 (total 6 H, s, OCH_3), 4.32 ($J = 3.7$ Hz) (1 H, d, position 4), 4.69 (1 H, s, position 2) and 5.07 ($J = 3.7$ Hz) (1 H, d, position 3) δ . Mass spectrum: 85 (100%), 103 (52%), 43 (38%), 45 (36%), 71 (28%), 115 (20%), 74 (19%), 87 (13%), and 101 (11%) *m/e*.

Trimethylsilyl derivative: To a solution of 10 mg of triol *X* in 1 ml of pyridine 0.2 ml of hexamethyldisilazane and 0.1 ml of trimethylchlorosilane were added and the mixture shaken for 30 s and allowed to stand for another 15 minutes at room temperature. On gas chromatography on a LKB-9000 apparatus with a 2 m column filled with SE-30 support the product appears to be pure; the inorganic salts present do not matter. Mass spectrum: characteristic ion ($M-90$)⁺, 334 *M/e*; further ionic species: 73 (100%), 260 (31%), 117 (24%), 191 (16%), 75 (14%), 133 (14%), 45 (13%), 89 (13%), 143 (12%), 58 (10%) and 43 (9%) *m/e*.

3-Acetyl-2,5-dimethoxy-3,4-diacetyloxetetrahydrofuran (IX)

A crude mixture of trihydroxy derivatives was acetylated by the method described for the preparation of compound III. A viscous liquid was obtained in 58% yield, b.p. $140^{\circ}\text{C}/0.2$ Torr which crystallised on standing. Crystallisation of 5.2 g of product from methanol at -35°C gave 3.2 g (61.5%) of ketone IX, m.p. $94-96^{\circ}\text{C}$. For $\text{C}_{12}\text{H}_{18}\text{O}_8$ (290.3) calculated: 49.65% C, 6.25% H, 17.38% OCH_3 ; found: 49.78% C, 6.38% H, 18.01% OCH_3 . Infrared spectrum: 890, 951, 986, 1006, 1046, 1101, 1158, 1220, 1246, 1376, 1430, 1736, 1768, 2835, 2925 and 2989

cm^{-1} . PMR spectrum: 2.02 (3 H, s, COCH_3), 2.15 and 2.31 (total 6 H, s, CH_3COO), 3.39 and 3.47 (total 6 H, s, CH_3O), 5.06 ($J = 3$ Hz) and 6.12 ($J = 3$ Hz) (d, AB system of protons in the positions 4 and 5) and 5.08 (1 H, s, position 2) δ .

3-(1-Acetoxyethyl)-2,5-dimethoxy-3,4-diacetyltetrahydrofuran (VIII)

From 21 g (0.1 mol) of acetal VI 12.2 g (55.5%) of a viscous material were obtained in the general manner. According to its composition the product corresponds to 3-(1-acetoxyethyl)-2,5-dimethoxy-3,4-dihydroxytetrahydrofuran (XI). In addition to this 2 g of compound VIII were regenerated. For $\text{C}_{10}\text{H}_{18}\text{O}_7$ (250.3) calculated: 47.99% C, 7.25% H, 24.80% OCH_3 ; found: 47.89% C, 7.25% H, 25.15% OCH_3 . Infrared spectrum: 1000, 1046, 1118, 1203, 1249, 1381, 1457, 1763, 2831, 2932, 2994, 3510 and 3578 cm^{-1} . Applying the acetylation procedure described for compound III to product XI triacetate VIII was obtained in 87% yield, b.p. 134–136°C/0.3 Torr. For $\text{C}_{14}\text{H}_{12}\text{O}_9$ (334.3) calculated: 50.30% C, 6.63% H, 18.57% OCH_3 ; found: 50.21% C, 6.67% H, 18.46% OCH_3 .

3-Acetyl-2,5-dimethoxy-3,4-dihydroxytetrahydrofuran (XIII)

To a solution of 0.5 g of sodium in 60 ml of methanol 2 g of diacetate IX were added and the mixture allowed to stand at room temperature for two days. It was then heated on a water bath for 30 minutes, cooled, and carbon dioxide was introduced into it for 2 hours. After evaporation of methanol the residue was dissolved in chloroform, the solution dried over sodium sulfate and evaporated. After dissolution of the residue in methanol and evaporation of the solvent in vacuum (1 Torr) the product crystallised out. Yield 1.6 g (64%) of 3-acetyl-2,5-dimethoxy-3,4-dihydroxytetrahydrofuran (XIII), m.p. 72–73°C (pentane). For $\text{C}_8\text{H}_{14}\text{O}_6$ (206.2) calculated: 46.60% C, 6.84% H, 23.91% OCH_3 ; found: 46.51% C, 6.80% H, 23.54% OCH_3 . Infrared spectrum: 946, 990, 1021, 1096, 1146, 1198, 1220, 1370, 1448, 1723, 2836, 2924, 3017, 3449 and 3570 cm^{-1} . PMR spectrum: 2.55 (3 H, s, CH_3CO), 3.29 and 3.40 (total 6 H, s, OCH_3), 3.63 (2H, OH), 4.70 (1 H, s, position 2), 4.55 ($J = 7$ Hz) and 4.85 ($J = 7$ Hz) (2 H, d, AB system in positions 4.5) δ .

3-(1-Hydroxyethyl)-2,5-dimethoxy-3,4-dihydroxytetrahydrofuran (Xa)

Using the foregoing procedure 4 g of triacetate VIII gave 2.8 g (96%) of isomeric mixture of triol Xa the IR spectrum of which was similar to the pure isomer X. For $\text{C}_8\text{H}_{16}\text{O}_6$ (208.2) calculated: 46.15% C, 7.79% H, 29.81% OCH_3 ; found: 46.25% C, 7.74% H, 29.62% COH_3 .

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