MONOMETHYL AND DIMETHYL ETHERS OF METHYL β-D-XYLOPYRANOSIDE

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The preparative advantages of partial methylation with subsequent separation of isomers over standard syntheses of individual derivatives are presented on the case of the methylation of methyl β-D-xylopyranoside (*I*). All seven possible methyl ethers were isolated in reasonable yields from a single reaction. Literature data concerning methyl 2,3-di-O-methyl-β-D-xylopyranoside (*V*) and methyl 2,4-di-O-methyl-β-D-xylopyranoside (*VI*) have been revised.

In connection with our studies of partial methylation of saccharides[1-5] we needed a larger amount of all monomethyl and dimethyl derivatives of methyl β-D-xylopyranoside (*I*). For our purposes the described syntheses of monomethyl ethers *II*, *III* and *IV*, *i.e.* both the nine-step synthesis[6] of methyl 2-O-methyl-β-D-xylopyranoside (*II*) from D-xylose (only 5% yield), or the three-step synthesis[7] of methyl 3-O-methyl-β-D-xylopyranoside (*III*) from xyloside *I* (only 7% yield), and the syntheses from the less accessible methyl β-D-arabinopyranoside (compound *III*, 5 steps, yield[8] 36%; compound *IV*, six steps, yield[9] 29%) were too lengthy. This is also true of the described syntheses of di-O-methyl derivatives, *V*, *VI* and *VII* (Table I). Partial methylation of methyl β-D-xylopyranoside (*I*) which when combined with a suitable separation technique could enable a substantially simpler, more efficient and direct preparation of the mentioned compounds, represented an attractive alternative. The results of Evtushenko and Ovodov[10] who studied the course of this reaction under some methylation conditions analytically by gas chromatography of corresponding acetates have shown that all isomers were present is such mutual ratios that the envisaged procedure should be feasible.

The methylation of methyl β-D-xylopyranoside (*I*) with methyl iodide in methanol in the presence of silver oxide gave a mixture of 8 substances, which was separated by preparative liquid chromatography on silica gel in the system chloroform–methanol (3%). In addition to the unreacted substance *I* and methyl 2,3,4-tri-O-methyl-β-D-xylopyranoside (*VIII*) three dimethyl derivatives were isolated, named A, B and C according to their increasing elution time, and three monomethyl derivatives, D, E and F. Practically no separation could be observed on current thin-layer chromatography for the pairs A and B or E and F, while in gas chromatography the reten-

tion times of all the isomers, A to F, were different; hence, the evaluation of the column chromatograph did not present any difficulty.

The melting point (lower-melting modification) and the optical rotation of the first eluted monomethyl derivative D (12%) differed from the literature data of all the three possible isomers (Table I). To this derivative, crystallizing in two modifications, we assigned the structure of methyl 4-O-methyl-β-D-xylopyranoside (*IV*) on the basis of the following facts. It can be detected with Bonner's reagent[11], which proves the presence of a vicinal diol grouping; the structure of 3-O-methyl derivative is thus excluded. Under the effect of acetic anhydride in pyridine it is converted to corresponding diacetyl derivative *IX*, with data considerably different from those in literature[6,12] given for the diacetate of the remaining possible 2-O-methyl isomer. A comparison of the values of the chemical shift of the proton H-4 (δ 3·42 ppm) in compound *IX* with the shifts for H-2 and H-3 (4·79 and 5·03 ppm) located the methoxyl

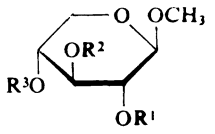
TABLE I

Melting points and optical rotations of methyl ethers of methyl β-D-xylopyranoside (*I*)

Derivative	Found		Described		
	m.p., °C (solvent)[a]	$[\alpha]_D$ (Chl)	m.p., °C (solvent)[a]	$[\alpha]_D$ (Chl)	ref.
II	110—111·5 (EA/P)	−69	111—112 (EA)	−67·7	6, 25
III	106—107 (EA/P)	−74 −65 (W)	102·5—103 (EA/P) 106—107 (EA/P)	−85·7 −66 (W)	8 7
IV	95—96 (EA/P)[b]	−98 −78 (W)	95 (E)	−69 (W)	9
V	59—61 (P)	−82	syrup[c] 63	−5·8[c] −47·3 (W)	6 24
VI	77—78 (P)	−70	77—78 (P) 60—61 (E/P)[d]	−70 −82·4[d]	7, 13, 26 6, 27
VII	88—89 (P)	−81	89—90 (E/P)[e]	−82·2 −71 (W)	6 9, 26
VIII	48—49 (subl.)	−71	49—50 (P)	−73 −66·6 (M)	9, 12, 13, 33 32

[a] E ether, Chl chloroform, EA ethyl acetate, P light petroleum, M methanol, W water, [b] The second crystal modification has m.p. 85—87°C (EA/P). [c] A syrup with b.p. 90—95°C (bath temp.) at 4 Pa, evidently a mixture of dimethylxylosides. [d] Incorrectly assigned structure; it is evidently 2,3-O-methyl isomer *V*. [e] Lit.[31] gives $[\alpha]_D$ −33° (Chl), −58°C (W) of this product, evidently a mixture of isomers.

group on the carbon atom $C_{(4)}$ unambiguously. The coupling constants ($J_{1,2}$ = = 7·1 Hz, $J_{2,3}$ = 8·9 Hz, $J_{3,4}$ = 8·8 Hz) confirmed its β-D-xylo configuration in a $^4C_1$ conformation. It should be noted that the melting point of methyl 2,3-di--O-acetyl-4-O-methyl-β-D-xylopyranoside (*IX*) also slightly differs from the described value[12].



I, $R^1 = R^2 = R^3 = H$
II, $R^1 = CH_3$; $R^2 = R^3 = H$
III, $R^1 = R^3 = H$; $R^2 = CH_3$
IV, $R^1 = R^2 = H$; $R^3 = CH_3$
V, $R^1 = R^2 = CH_3$; $R^3 = H$
VI, $R^1 = R^3 = CH_3$; $R^2 = H$
VII, $R^1 = H$; $R^2 = R^3 = CH_3$
VIII, $R^1 = R^2 = R^3 = CH_3$
IX, $R^3 = CH_3$; $R^1 = R^2 = COCH_3$
X, $R^2 = R^3 = COCH_3$; $R^1 = CH_3$
XI, $R^1 = R^3 = COCH_3$; $R^2 = CH_3$
XII, $R^1 = R^2 = CH_3$; $R^3 = p\text{-}CH_3C_6H_4SO_2$
XIII, $R^1 = R^3 = CH_3$; $R^2 = p\text{-}CH_3C_6H_4SO_2$

The structure of methyl 2-O-methyl-β-D-xylopyranoside (*II*) must naturally correspond to monomethyl ether E (22%), which is also cleaved with periodate in contrast to the remaining isomer F. The physical properties of *II* are identical with the data of the substance, presented in literature (Table I). On acetylation it gave 3,4-di--O-acetyl derivative *X* with properties corresponding to methyl 3,4-di-O-acetyl--2-O-methyl-β-D-xylopyranoside from ref.[12]. We were unable by any attempt at crystallization to prepare the form with the melting point 78–79°C, given in the literature[6]. The structure of methyl 3-O-methyl-β-D-xylopyranoside (*III*) for compound F (19%), which cannot be cleaved with sodium periodate, was confirmed by its conversion to methyl 2,4-di-O-acetyl-3-O-methyl-β-D-xylopyranoside (*XI*) with properties identical with those of the substance described in literature[12].

The separation of isomeric monomethyl ethers *II* and *III* is difficult. During ordinary low-pressure liquid chromatography on silica gel, the ratio of *II* and *III* in the fractions changes from 99 : 1 to 15 : 85 (according to GLC); a further repeated chromatography affords a considerable part of 2-O-methyl derivative *II* in pure form, but the isolation of pure isomer *III* by chromatography alone is more difficult. Nevertheless, the absence of the vicinal diol grouping in 3-O-methyl derivative *III* permits the isolation of even this compound in pure form without the need of using HPLC. The chromatographically easily accessible mixture of *II* and *III* (in a 1 : 4 ratio) was submitted to periodate cleavage and compound *III* was separated from the reaction product of *II* by filtration through a silica gel layer. The periodate cleavage can also be used for the crude methylation mixture; thus, using the combination of methylation and the cleavage pyranoside *III* can be prepared in a single reaction

step in 20% yield by simple chromatography (starting glycoside *I* and isomers *II* and *IV* are decomposed).

For an unambiguous assignment of structures to dimethyl derivatives, A, B and C (eluted from the column in the given order), we used the results of partial methylations of individual isolated monomethyl derivatives *II*–*IV*. Dimethyl derivative A (7%), formed both during the methylation of methyl-3-O-methyl-β-D-xylopyranoside (*III*) and of methyl 4-O-methyl-β-D-xylopyranoside (*IV*) has regularly the structure of methyl 3,4-di-O-methyl-β-D-xylopyranoside (*VII*). On further methylation it gives methyl 2,3,4-tri-O-methyl-β-D-xylopyranoside (*VIII*). Dimethyl derivative B (11%) was identical with the product which was formed in the methylation of 2-O-methyl-xyloside *II* and 4-O-methyl-xyloside *IV*, the further methylation of which led to the persubstituted glycoside *VIII*. Hence, the structure of methyl 2,4-di-O-methyl--β-D-xylopyranoside (*VI*) was assigned to compound B. The separation of isomers *VI* and *VII* by column chromatography on silica gel is incomplete; the ratio of compounds *VII* and *VI* in fractions changes according to GLC from about 70 : 30 to 15 : 85. However, they can be obtained in pure state and in satisfactory yield by repeated chromatography. The excellent crystallization ability of the 2,4-di-O-methyl isomer *VI* also can be used for the separation; one crystallization of a mixture containing up to 30% of the isomer *VII* from light petroleum gives a pure product. This is in agreement with the fact that Wintersteiner and Klingsberg isolated it[13] by direct crystallization of the crude methylation mixture of compound *I*. The remaining isomer C (6%) was assigned the structure of methyl 2,3-di-O-methyl-β-D-xylopyranoside (*V*). It is a product of methylation both of monomethyl derivative *II* and *III*.

The physical constants of dimethyl derivatives differ from the data in literature (Table I) substantially more than in the case of monomethyl derivatives. Considering they are standard compounds used in structural analysis of polysaccharides, any doubts about their structure, melting points and optical rotations would be out of place. Methyl 2,3-di-O-methyl-β-D-xylopyranoside (*V*) isolated from the methylation mixture of compound *I* in a crystalline state is certainly a completely different substance from the syrup to which this structure has been assigned in literature[6]. Its method of preparation from permethylated xylan by hydrolysis and Koenigs–Knorr reaction permits, in our opinion, the formation of a mixture of di-O-methyl-xylosides, which could possess the mentioned properties. The data for its crystalline 4-O-*p*-toluensulfonyl derivative[6] (*cf.* compound *XII*) are also incorrect; it may represent the corresponding α-anomer so far undescribed in literature. Similar mixtures of di-O-methylxylosides are obtained from permethylated xylan even in the case of methanolysis[14–25], where a crystalline substance was isolated in one case[24] chromatographically in a 0·5% yield, having identical properties with our product.

The data for methyl 2,4-di-O-methyl-β-D-xylopyranoside (*VI*) are identical with the data published for a substance obtained already in 1929 by fractional crystallisation

of the methylation mixture of glycoside *I* with dimethyl sulfate and sodium hydroxide[13]. The same compound was also prepared by Ferrier and coworkers[7] from methyl 3-O-(N-phenylcarbamoyl)-β-D-xylopyranoside, and Kováč and Hirsch[26] from 3-O-benzyl-1,2-O-isopropylidene-α-D-glucofuranose. The assumed second modification[6,7,27] of compound *VI* could not be prepared by us in spite of our efforts; however the data for this modification are strikingly similar to the data for crystalline *V*. In the intention to support this assumption we converted out dimethyl ether *V* to the corresponding 4-O-*p*-toluenesulfonyl derivative *XII*; its physical constants are also identical with the data of the assumed methyl 2,4-di-O-methyl--3-O-*p*-toluenesulfonyl-β-D-xylopyranoside[6] and they differ completely from the *p*-toluenesulfonyl ester *XIII*, prepared by esterification of *VI*.

The seven-step synthesis[6] leading to the mentioned crystal modification of compound *VI* (the possibility of the incorrectness of this synthesis has been mentioned in ref.[13,26]) starts from pyranoside *I*, it includes partial tritylation, acetylation of the remaining hydroxyl groups, replacement of the trityl group for a nitrate one, deacetylation, methylation and eventually elimination of the protecting nitrate group in the position 3. From the present view it cannot be excluded that already in the first reaction step, *i.e.* partial tritylation of secondary hydroxyl group, the true product was 4-O-tritylxyloside and not the expected 3-O-tritylxyloside. Further steps, excluding any migration of the groups, would then lead to the isolation of 2,3-dimethyl ether instead of 2,4-dimethyl ether. The second synthesis leading to this modification[27] starts from diethyl mercaptal of D-xylose which should have given 2,4:3,5-di-O-isopropylidene derivative exclusively on reaction with acidified acetone. The selective splitting off of the 2,4-acetal protecting group during the methylation of this compound finally led (after conversion to glycoside) to the alleged methyl 2,4-di-O-methyl-β-D-xylopyranoside. However it was shown later[28-30] that under the conditions used for acetal formation the product is 2,3:4,5-di-O-isopropylidene isomer the acetal groups of which are resistent to methylation[28]. However, it cannot be excluded that the syrupy reaction product of diethyl mercaptal with acetone, prepared by Dalley and McIlroy[27], was a mixture of 4,5-O-isopropylidene- and 2,3:4,5-di-O-isopropylidene derivative (a comparison of the optical rotation values with those of pure acetals[29] also indicates this view) of which the first mentioned finally afforded the pyranoside *V* considered by us. The second possible explanation consisting in partial solvolysis of 2,3-acetal in the diisopropylidene derivative under the effect of moisture during methylation (see the cleavage of 2,4-acetal mentioned above[27]) also leading eventually to 2,3-dimethyl derivative *V*, is excluded; in 2,3:4,5--di-O-isopropylidene derivative the acetal group in the position 4,5 is split off first in acid medium[30].

In comparison with the decribed syntheses[6,7] also starting from D-xylose, partial methylation followed by liquid chromatography on a silica gel column is more advantageous for any of the three monomethyl ethers *II*, *III* and *IV*, both from

the point of view of time and that of yield. The time criterion is also applicable in comparison with multistep syntheses based on the less accessible D-arabinose[8,9]. Moreover, partial methylation affords all isomers simultaneously and in comparable yields. In dimethyl derivatives the most favourable of the described syntheses[6,26,31] of methyl 3,4-di-O-methyl-β-D-xylopyranoside (*VII*) consists of seven reaction steps and it gives a yield of 3% (ref.[26]), while the synthesis of 2,4-di-O-methyl derivative *VI* from D-glucose consists of as many as ten steps[26], giving approximately 1% yield. Even though it requires a somewhat complicated chromatographic separation (preparative gas chromatography of the mixture of di-O-methyl derivatives also can be used), the partial methylation is much more advantageous for the preparation of these two compounds; on increasing the degree of substitution the yield of both isomers *VI* and *VII*, can be improved to about 20%. The remaining 2,3-dimethyl ether *V* can be isolated in pure form easily by liquid chromatography.

The procedure used for the preparation of methyl ethers is more advantageous than the preparative gas chromatography of corresponding acetates[12]. Two excessive reaction steps (acetylation, deacetylation), together with the time-consuming separation of eight compounds faced us with complications when working with larger amounts. In addition the fully acetylated derivatives are so volatile, that losses cannot be prevented during the working up, similarly as in the case of methyl 2,3,4-tri-O-methyl-β-D-xylopyranoside[13,15] (*VIII*).

EXPERIMENTAL

The melting points were determined on a Kofler block and they are not corrected. Optical rotations were determined on an Opton PPP 0·005 polarimeter at 20°C and 1·0 concentration. Column chromatographies were carried out on silica gel Lachema 100—160 μm, thin-layer chromatography on silica gel G according to Stahl (Merck, Darmstadt), 10—40 μm, on layers of 75 × 25 × 0·2 mm dimensions. Chloroform with 3% of methanol was used as developing solvent. Substances were detected by spraying with a 1% solution of cerium-IV-sulfate in 10% sulfuric acid and mineralization. Gas chromatography was carried out on a Varian-Aerograph 2100 instrument with flame-ionization detector in combination with a Hewlett-Packard 3380A integrator. Nitrogen was the carrier gas, flow-rate 30 ml/min. A glass column of 2 mm diameter and 1 800 mm long was packed with 0·5% Tridox on Varaport 30 (100—120 mesh), the temperature was programmed: 4°C/min in the 120—170°C interval. Temperature of the injector was 190°C, of the detector 200°C. Retention times of the methyl ethers were the following: *VIII* 4·75 min, *V* 9·21 min, *VI* 9·86 min, *VII* 10·22 min, *III* 11·78 min, *II* 13·48 min, *IV* 14·37 min. The solvents were evaporated on a rotational evaporator under reduced pressure (water pump) at maximum 35°C bath temperature. The ^{1}H NMR spectra were measured in deuteriochloroform on a Varian XL-100-15 instrument, the chemical shifts (in δ) are referred to tetramethylsilane as internal reference. The coupling constant values (in Hz) are obtained from the analyses of first order spectra.

Methylation of Pyranoside *I*

A mixture of 2·0 g of methyl β-D-xylopyranoside[34] (*I*), 7·6 ml of methyl iodide, 40 ml of methanol

and 4·0 g of silver oxide was stirred at room temperature (*cf.* refs[10,12,35]). The reaction course was monitored by thin-layer chromatography. A chloroform methanol mixture (with 3% of methanol) was found best for our study and it could discern 5 compounds in addition to compound *I* Gas chromatography could detect seven substances different from *I*. After 4 h stirring the mixture was filtered, the solid material washed with methanol (3 times 10 ml) and the combined filtrates evaporated to a syrup (2·4 g) which was made up with chloroform to 10 ml. After inoculation and standing at 10°C 0·3 g (15%) of compound *I* crystallized out, the mother liquors were evaporated and chromatographed on a silica gel column (25 × 2 cm). The fractions (10 ml each) were tested by thin-layer chromatography and gas chromatography. Mixed fractions were rechromatographed under the same conditions. The compounds were eluted from the column in the following order: *VIII*, *VII*, *VI*, *V*, *IV*, *II*, *III* and *I*.

Methyl 2,3,4-*tri*-O-*methyl*-β-D-*xylopyranoside* (VIII), 49 mg, 2%, volatilizes already during the evaporation of the solvents. A sample for analysis was sublimated at 2·0 kPa and 40°C (bath temperature). For data see Table I. For $C_9H_{18}O_5$ (206·2) calculated: 52·41% C, 8·80% H; found: 52·36% C, 8·94% H.

Methyl 3,4-*di*-O- *methyl*-β-D-*xylopyranoside* (VII) was isolated in pure form by repeated chromatography of the fractions which in addition to it also contained compound *VI*. The R_F values of these two isomers were almost identical in thin-layer chromatography. Compound *VII* (164 mg, 7%) was crystallized from light petroleum (b.p. 45—60°C) and sublimated at 13 Pa and 60°C (bath temperature). For data see Table I. For $C_8H_{16}O_5$ (192·2) calculated: 49·99% C, 8·39% H; 50·16% C, 8·56% H.

Methyl 2,4-*di*-O-*methyl*-β-D-*xylopyranoside* (VI), 256 mg, 11%, was crystallized from light petroleum (45—60°C). Crystalization from this solvent also permits its separation from mixtures containing the isomer *VII*. A sample with the same melting point also could be obtained by repeated crystalization from a mixture of ether and light petroleum (see data in Table I). For $C_8H_{16}O_5$ (192·2) calculated: 49·99% C, 8·39% H; found: 50·16% C, 8·56% H.

Methyl 2,3-*di*-O-*methyl*-β-D-*xylopyranoside* (V), 140 mg, 6%, crystallized during distillation (7 Pa, 120°C bath temp.). For analysis it was crystallized from light petroleum (45—60°C). For data see Table I. For $C_8H_{16}O_5$ (192·2) calculated: 49·99% C, 8·39% H; found: 50·47% C, 8·05% H.

Methyl 4-O-*methyl*-β-D-*xylopyranoside* (IV), 263 mg, 12%, was crystallized from a mixture of ethyl acetate and light petroleum (m.p. 45—60°C). It crystallizes in two modifications having the same optical rotation value and elemental analysis, for data see Table I. For $C_7H_{14}O_5$ (178·2) calculated: 47·19% C, 7·92% H; found: 47·55% C, 8·14% H.

Methyl 2-O-*methyl*-β-D-*xylopyranoside* (II), 471 mg, 22%, was obtained by repeated chromatography of fractions containing also isomer *III*. The R_F values of these two isomers are almost identical in thin-layer chromatography. Compound *II* was crystallized from a mixture of ethyl acetate and light petroleum (Table I). For $C_7H_{14}O_5$ (178·2) calculated: 47·19% C, 7·92% H; found: 47·55% C, 7·93% H.

Methyl 3-O-*methyl*-β-*D*-*xylopyranoside* (III), 410 mg, 19%, was isolated by repeated chromatography of the fractions also containing isomer *II*. Compound *III* was crystallized from a mixture of ethyl acetate and light petroleum (Table I). For $C_7H_{14}O_5$ (178·2) calculated: 47·19% C, 7·92% H; found: 47·28% C, 7·98% H.

Applying the system chloroform–methanol 10% for elution 35 mg (2%) of unreacted compound *I* were eluted.

Methyl 3-O-Methyl-β-D-xylopyranoside (*III*)

a) Pyranoside *I*, 3·00 g, was methylated and worked up in the same manner as described above. The fraction (578 mg) of a mixture of 3-O-methyl derivative *III* and 2-O-methyl derivative *II* in a 4 : 1 ratio, obtained from the first column chromatography on silica gel was dissolved in 3 ml of water, 780 mg of sodium periodate were added and the mixture stirred at room temperature for 2 h. The salts were precipitated by addition of 50 ml of ethanol, washed with three 15 ml portions of ethanol and the combined filtrates were evaporated. The residual syrup (664 mg) was filtered through a column of silica gel using a mixture of chloroform and 2% of methanol. The fractions containing pure pyranoside *III* were combined, evaporated (417 mg) and crystallized from a mixture of ethyl acetate and light petroleum. Its properties were identical with those of the product isolated above.

b) Pyranoside *I*, 2·0 g, was methylated as described above. After filtration and evaporation of the solvents the mixture was dissolved in 4 ml of water, 1·0 g of sodium periodate was added and the mixture stirred at room temperature for 2 h. After addition of 75 ml of methanol the precipitated salts were filtered off and washed with three 15 ml portions of methanol. The combined filtrates were evaporated and the residue chromatographed on a silica gel column, giving in addition to compounds *V*, *VI* and *VII* (490 mg) also 450 mg (21%) of pyranoside *III*.

Methylation of Pyranoside *III*

A mixture of 220 mg of methyl ether *III*, 4 ml of methyl iodide, 4 ml of acetonitrile and 1·5g of silver oxide was stirred at room temperature for 5 h. After filtration, washing of the solid material with three 10 ml portions of methanol, and evaporation of the combined filtrates the residual syrup was chromatographed on a silica gel column (25 × 2 cm). Yield, 46 mg (19%) of 2,3-di-O-methyl derivative *VI* and 54 mg (23%) of 3,4-di-O-methyl derivative *VII*, the m.p., $[\alpha]_D$ and retention times were identical with the data of the substances isolated above.

Methylation of Pyranoside *II*

Methyl ether *II* (212 mg) was methylated and chromatographed in the same manner as given for compound *III*. Yield, 80 mg (35%) of 2,4-di-O-methyl derivative *VII* and 64 mg (28%) of 2,3-di-O-methyl derivative *V* with the m.p., $[\alpha]_D$ and retention times identical with the data given for the substances isolated above.

Methylation of Pyranoside *IV*

A mixture of 4·5 mg of compound *IV*, 0·4 ml of methyl iodide, 0·4 ml of acetonitrile and 100 mg of silver oxide was shaken at room temperature and the reaction course was checked by gas chromatography. In addition to the starting compound *IV* and the tri-O-methyl derivative *VIII*, the mixture contained two dimethyl derivatives with the retention times identical with those of 2,4-O-methyl derivative *VI* and 3,4-di-O-methyl derivative *VII*, isolated above.

Methyl 2,3-Di-O-acetyl-4-O-methyl-β-D-xylopyranoside (*IX*)

A mixture of 72 mg of *IV*, 0·9 ml of pyridine and 0·5 ml of acetic anhydride was allowed to stand at room temperature for 20 h. After decomposition with water, evaporation, dissolution in benzene (10 ml) and repeated evaporation 103 mg of crystalline compound *IX* were obtained which were recrystallized from light petroleum (b.p. 60–70°C). M.p. 125–126°C, $[\alpha]_D$ −82° (chloroform), lit.[12] gives m.p. 119–121°C, $[\alpha]_D$ −80·2° (chloroform). ^{1}H NMR data; 5·03 (1 H, dd,

$J_{2,3}$ = 8·9 Hz, $J_{3,4}$ = 8·8 Hz, H-3), 4·79 (1 H, dd, $J_{1,2}$ = 7·1, $J_{2,3}$ = 8·9, H-2), 4·31 (1 H, d, $J_{1,2}$ = 7·1, H-1), 4·09 (1 H, dd, $J_{4,5e}$ = 5, $J_{5a,5e}$ = −11·5, H-5e), 3·42 (1 H, m, H-4), 3·25 (1 H, dd, $J_{4,5a}$ = 9, $J_{5a,5e}$ = −11·5, H-5a), 3·44 (3 H, s, CH_3O), 3·39 (3 H, s, CH_3O), 2·05 (6 H, s, 2 × CH_3CO). For $C_{11}H_{18}O_7$ (262·3) calculated: 50·38% C, 6·92% H; found: 50·47% C, 7·05% H.

Methyl 3,4-Di-O-acetyl-2-O-methyl-β-D-xylopyranoside (*X*)

Methyl derivative *II* (85 mg) was acetylated in the same manner as isomer *IV*. After crystallization from light petroleum (b.p. 60—70°C) 106 mg (84%) of acetyl derivative *X* were obtained, m.p. 93—94·5°C, $[\alpha]_D$ −38° (chloroform), lit[6,12] gives m.p. 94—95°C, $[\alpha]_D$ −38·1° (chloroform).

Methyl 2,4-Di-O-acetyl-3-O-methyl-β-D-xylopyranoside (*XI*)

A mixture of 58 mg of compound *III*, 0·8 ml of pyridine and 0·5 ml of acetic anhydride was allowed to stand at room temperature for 20 h and worked up equally as in the preparation of compound *IX*. After crystallization from light petroleum (b.p. 60—70°C) 60 mg (70%) of analytically pure compound *XI* were obtained, m.p. 87—88°C $[\alpha]_D$ −81° (chloroform), lit.[12] gives m.p. 86—88°C, $[\alpha]_D$ −77·5° (chloroform).

Methyl 2,3-Di-O-methyl-4-O-*p*-toluenesulfonyl-β-D-xylopyranoside (*XII*)

A mixture of 30 mg of compound *V*, 0·3 ml of pyridine and 200 mg of *p*-toluenesulfonyl chloride was allowed to stand at room temperature for 4 days. After partitioning of the mixture between water and chloroform, evaporation of the organic layer and crystallization from light petroleum (60—70°C) 46 mg (85%) of the *p*-toluenesulfonyl derivative *XII* were obtained, m.p. 88—89°C, $[\alpha]_D$ −60 (chloroform). Lit.[6] gives m.p. 56—69°C, $[\alpha]_D$ −8·8° (chloroform). Evidently the English authors had a mixture of anomers. For $C_{15}H_{22}O_7S$ (346·3) calculated: 52·02% C, 6·40% H; found: 51·88% C, 6·62% H.

Methyl 2,4-Di-O-methyl-3-O-*p*-toluenesulfonyl-β-D-xylopyranoside (*XIII*)

Dimethyl derivative *VI* (38 mg) was esterified in the same manner as in the preparation of compound *XII*. Yield, 52 mg (76%) of ester *XIII*, m.p. 75—77°C, $[\alpha]_D$ −28° (chloroform). Literature[13] gives m.p. 75—76°C, $[\alpha]_D$ +28·8° (chloroform), or also[6] m.p. 88°C, $[\alpha]_D$ −58·9° (chloroform). In the second case evidently the isomer *XII* was obtained while in the first case the sign of the optical rotation is erroneously positive. For $C_{15}H_{22}O_7S$ (346·3) calculated: 52·02% C, 6·40% H; found: 52·13% C, 6·55% H.

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