PARTIAL ALKYLATION OF DEOXYSUGARS. PREPARATION OF METHYL ETHERS OF METHYL 4,6-DIDEOXY-α-D-*xylo*-HEXOPYRANOSIDE AND METHYL 4,6-DIDEOXY-α-L-*lyxo*-HEXOPYRANOSIDE

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Received October 13th, 1972

On methylation of methyl 4,6-dideoxy-α-D-*xylo*-hexopyranoside (*I*) and methyl 4,6-dideoxy-α-L-*lyxo*-hexopyranoside (*V*) with methyl iodide and sodium hydroxide in dimethylformamide a mixture of monosubstituted and disubstituted ethers, *II, III, IV* and *VI, VII, VIII*, respectively, was obtained, which was separated by preparative column or gas chromatography. The structure of the monomethyl ethers was proved by nuclear magnetic resonance and mass spectrometry. Acid hydrolysis of the above mentioned methyl ethers gave corresponding aldoses *IX*—*XIV* of which 4,6-dideoxy-3-O-methyl-D-*xylo*-hexose (*X*) was identical with the natural chalcose.

The synthesis of partially methylated sugar derivatives is usually complicated by the necessity of a preliminary preparation of intermediates with suitably protected hydroxyl groups, with the exception of that to be etherified. With the help of modern separation methods this process may be sometimes circumvented and the required substances isolated from the mixture obtained by direct methylation of the unprotected glycoside, if the reaction was carried out under the conditions favourable for the formation of partially methylated derivatives. This procedure is suitable especially if it is necessary to prepare all methyl ethers which can arise on methylation of a given glycoside.

In our case, for the investigation of the chemistry of sugar lactones, we needed methyl ethers of methyl 4,6-dideoxy-α-D-*xylo*-hexopyranoside (*I*) and methyl 4,6-dideoxy-α-L-*lyxo*-hexopyranoside (*V*). Both glycosides, prepared by known procedures[1,2] were submitted to reaction with methyl iodide in dimethylformamide in the presence of a 1,2-molar amount of powdered sodium hydroxide. The reaction mixture from the methylation of glycoside *I*, containing approximately 17% of the starting compound, 38·5% of methyl 4,6-dideoxy-2-O-methyl-α-D-*xylo*-hexopyranoside (*II*), 10% of methyl 4,6-dideoxy-3-O-methyl-α-D-*xylo*-hexopyranoside (*III*), and 26% of methyl 4,6-dideoxy-2,3-di-O-methyl-α-D-*xylo*-hexopyranoside (*IV*), could be separated either by preparative column chromatography on silica gel, or (after preliminary chromatographic separation of the strating material) by prepara-

tive gas chromatography. The reaction mixture from the methylation of glycoside *V*, containing approximately 16% of the starting compound, 29% of methyl 4,6-dideoxy-2-O-methyl-α-L-*lyxo*-hexopyranoside (*VI*), 13% of methyl 4,6-dideoxy-3-O-methyl-α-L-*lyxo*-hexopyranoside (*VII*), and 15% of methyl 4,6-dideoxy-2,3-di-O-methyl-α-L-*lyxo*-hexopyranoside (*VIII*) was separated by preparative column chromatography on alumina.*

The position of the methyl group in monomethyl ethers *II*, *III*, *VI*, and *VII* was determined on the basis of their mass and PMR spectra. The mass spectra of 2-O-methyl derivatives *II* and *VI* contained a signal of *m/e* 88 assigned[3] to the fragment $CH_3O—\dot{C}H—CH=\overset{+}{O}CH_3$, which was not present in the spectra of 3-O-methyl derivatives *III* and *VII*. In the PMR spectra of methyl ethers *II* and *III* the signals of protons bound to the carbon carrying the free hydroxy group were shifted as against the signals of the corresponding protons of the disubstituted derivative *IV* by about 0·25–0·40 p.p.m. downfield. A similar shift may be observed when the δ-values of protons $H_{(2)}$ or $H_{(3)}$ in the spectra of methyl ethers *VI* and *VII* are compared, in which the position of the hydroxy group is determined unambiguously by decoupling experiments (for this purpose the spectra were measured at −70°C). On the basis of the values of the observed coupling constants the conformation with axial anomeric methoxyl group may be assigned to all substances measured.

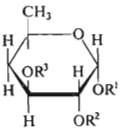
Monomethyl derivative *III*, having an optical rotation close to the value given for it in the literature[4], gave on hydrolysis 4,6-dideoxy-3-O-methyl-D-*xylo*-hexose (*X*) the melting point and the specific rotation of which correspond to the values of the described[5,6] natural chalcose (lankavose). Also all other mono- and disubstituted glycosides were submitted to acid hydrolysis and the corresponding aldoses were thus obtained: crystalline 4,6-dideoxy-2-O-methyl-D-*xylo*-hexose (*IX*) and 4,6-dideoxy-3-O-methyl-L-*lyxo*-hexose (*XIII*), and syrupy 4,6-dideoxy-2-O-methyl-L-*lyxo*-hexose (*XII*), 4,6-dideoxy-2,3-di-O-methyl-D-*xylo*-hexose (*XI*), and 4,6-dideoxy-2,3-di-O-methyl-L-*lyxo*-hexose (*XIV*).

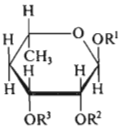
The mentioned preparation procedure for partially methylated sugars appreciably simplifies their syntheses, as may be demonstrated on the example of chalcose which was already synthetised in the past by several routes[4,7–10]. Should the described reaction be evaluated from the theoretical point of view it may be stated that the quantitative representation of the components in the reaction mixtures after the methylation of glycosides *I* and *V* corresponds in principle, to the known facts[11–15] about the increased reactivity of the hydroxyl group on the second carbon of the sugar chain toward methylation agents.

* The percentual composition of the reaction mixture is given on the basis of the yields determined by preparative chromatography. The resulting incomplete balance is probably due to the appreciable volatility of disubstituted derivatives *IV* and *VIII*, which might have caused losses during the purification and the chromatographic separation.

EXPERIMENTAL

The melting points were measured on a Kofler block and they are not corrected. Optical rotation was determined on an Opton apparatus with a subjective reading. The mass spectra were measured on a LKB 9000 spectrometer. PMR spectra were recorded on a Varian XL-100 apparatus in $CDCl_3$, using tetramethylsilane as internal standard, unless otherwise stated. For chromatographic analyses on thin layers microplates with silica gel G (Merck, Darmstadt, GFR) or with non-adhering alumina (Reanal, Budapest, act. II—III) were used. Developing solvents were chloroform–methanol 100 : 5 (S_1), chloroform–methanol 100 : 10 (S_2), benzene–ethanol 100 : 5 (S_3); detection by spraying with 1% cerium-IV sulfate in 10% sulfuric acid and subsequent heating, or exposure to iodine vapours.





I; $R^1 = CH_3$, $R^2, R^3 = H$
II; $R^1, R^2 = CH_3$, $R^3 = H$
III; $R^1, R^3 = CH_3$, $R^2 = H$
IV; $R^1, R^2, R^3 = CH_3$
IX; $R^1, R^3 = H$, $R^2 = CH_3$
X; $R^1, R^2 = H$, $R^3 = CH_3$
XI; $R^1 = H$, $R^2, R^3 = CH_3$

V; $R^1 = CH_3$, $R^2, R^3 = H$
VI; $R^1, R^2 = CH_3$, $R^3 = H$
VII; $R^1, R^3 = CH_3$, $R^2 = H$
VIII; $R^1, R^2, R^3 = CH_3$
XII; $R^1, R^3 = H$, $R^2 = CH_3$
XIII; $R^1, R^2 = H$, $R^3 = CH_3$
XIV; $R^1 = H$, $R^2, R^3 = CH_3$

Partial Methylation of Methyl 4,6-Dideoxy-α-D-*xylo*-hexopyranoside

Into a solution of glycoside *I* (3·1 g, 20 mmol, ref.[1]) in 25 ml dimethylformamide and 5·6 ml of methyl iodide (90 mmol) powdered sodium hydroxide (946 mg, 24 mmol) was added at −10°C under stirring, over 20—30 minutes. The mixture was stirred at room temperature for 24 hours and the reaction followed by thin-layer chromatography on silica gel G in system S_1 where the starting compound had R_F 0·19, 2-O-methyl derivative *II* R_F 0·34, 3-O-methylderivative *III* R_F 0·36, and di-O-methyl derivative *IV* R_F 0·53. The reaction mixture was extracted from aqueous solution (100 ml), which was previously saturated with sodium chloride, with chloroform. The chloroform extract was dried and evaporated and the residue was freed from the remains of dimethylformamide by drying in a vacuum (oil pump) at a temperature not exceeding 50°C. The obtained mixture of substances (3·3 g) was separated chromatographically on silica gel CH (150 g) with benzene–ethanol 0—10%; or it was liberated from the starting material by a rapid chromatography on 50 g of silica gel CH (elution with benzene–ethanol) and the remaining mixture of monomethyl ethers *II*, *III* and *IV* was then separated by preparative gas chromatography. Using both these procedures the following substances were isolated from the mixture in addition to approximately 17% of the starting glycoside *I*:

Methyl 4,6-*dideoxy*-2-O-*methyl*-α-D-xylo-*hexopyranoside* (II), yield 38·5%, syrup, boiling at 70°C/0·01 Torr (bath temperature), $[\alpha]_D^{24} + 177 \pm 1°$ (*c* 1·2, chloroform); PMR (the signals were assigned using integral curves, decoupling and INDOR experiments; coupling constants are given with ±0·5 Hz precision): H_1: 4·88 p.p.m., $J_{1,2} = 3{\cdot}5$ Hz; H_2: 3·08 p.p.m., $J_{2,1} = 3{\cdot}5$ Hz, $J_{2,3} = 9$ Hz; H_3: 3·98 p.p.m., $J_{3,2} = 9$ Hz, $J_{3,4e} = 5$ Hz, $J_{3,4a} = 11{\cdot}5$ Hz; H_{4e}: 2·0 p.p.m., $J_{4e,3} = 5$ Hz, $J_{4e,4a} = 13{\cdot}5$ Hz, $J_{4e,5} = 2{\cdot}5$ Hz; H_{4a}: 1·37 p.p.m., $J_{4a,3} = 11{\cdot}5$ Hz, $J_{4a,4e} =$

= 13·5 Hz, $J_{4a,5}$ = 11·5 Hz; H_5: 3·6 — 4·15 p.p.m.; H_6: 1·20 p.p.m., $J_{6,5}$ = 6·5 Hz; OCH_3: 3·41 p.p.m., 3·48 p.p.m. For $C_8H_{16}O_4$ (176·2) calculated: 54·53% C, 9·15% H; found 54·49% C, 9·23% H.

Methyl 4,6-*dideoxy*-3-O-*methyl*-α-D-xylo-*hexopyranoside* (III), yield 10%, syrup, b.p. 80°C/0·1 Torr; $[\alpha]_D^{25}$ +194·5 ± 1° (*c* 0·6, chloroform); PMR H_1: 4·71 p.p.m., $J_{1,2}$ = 3·5 Hz; H_2: approx. 3·41 p.p.m.; H_3: approx. 3·44 p.p.m.; H_{4e}: 2·03 p.p.m., $J_{4e,3}$ = 4·5 Hz, $J_{4e,4a}$ = 13·5 Hz, $J_{4e,5}$ = 2·5 Hz; H_{4a}: 1·16 p.p.m., $J_{4a,3}$ = 11·5 Hz, $J_{4a,4e}$ = 13·5 Hz, $J_{4a,5}$ = 11·5 Hz H_5: 3·83 p.p.m., $J_{5,4a}$ = 11·5 Hz, $J_{5,4e}$ = 2·5 Hz, $J_{5,6}$ = 6·5 Hz; H_6: 1·15 p.p.m., $J_{6,5}$ = 6·5 Hz; OCH_3: 3·40 and 3·43 p.p.m.; For $C_8H_{16}O_4$ (176·2) calculated: 54·53% C, 9·15% H; found: 54·60% C, 9·28% H. Literature[4] data for this substance: $[\alpha]_D^{20}$ +184·5° (chloroform).

Methyl 4,6-*dideoxy*-2,3-*di*-O-*methyl*-α-D-xylo-*hexopyranoside* (IV), yield 26%, syrup, b.p. 63°C/1 Torr; $[\alpha]_D^{22}$ +172 ± 1° (*c* 0·72, chloroform); PMR: H_1: 4·82 p.p.m., $J_{1,2}$ = 3·5 Hz; H_2: 3·16 p.p.m., $J_{2,1}$ = 3·5 Hz, $J_{2,3}$ = 9 Hz; H_3: 3·57 p.p.m., $J_{3,2}$ = 9 Hz, $J_{3,4e}$ = 5 Hz, $J_{3,4a}$ = 11·5 Hz; H_{4e}: 2·08 p.p.m., $J_{4e,3}$ = 5 Hz, $J_{4e,4a}$ = 13·5 Hz, $J_{4e,5}$ = 2·5 Hz; H_{4a}: 1·22 p.p.m., $J_{4a,3}$ = 11·5 Hz, $J_{4a,4e}$ = 13·5 Hz, $J_{4a,5}$ = 11·5 Hz; H_5: 3·55—4·15 p.p.m.; H_6: 1·19 p.p.m., $J_{6,5}$ = 6·5 Hz; OCH_3: 3·40, 3·43 and 3·50 p.p.m.. For $C_9H_{18}O_4$ (190·2) calculated: 56·82% C, 9·53% H; found: 57·07% C, 9·66% H. In the literature[16] the β-anomer of this substance is described with $[\alpha]_D^{23}$ −30° (tetrachloromethane).

Partial Methylation of Methyl 4,6-dideoxy-α-L-*lyxo*-hexopyranoside (*V*)

Glycoside *V* (8 mg, 5 mmol, ref.[2]) was dissolved in 8 ml of dimethylformamide and submitted to methylation with 1·7 ml (27 mmol) of methyl iodide and 240 mg (6 mmol) of powdered sodium hydroxide under the conditions analogous to that in the preceding experiment. The mixture of substances obtained after working up of the reaction mixture (chloroform extract) was separated on a column of 50 g of alumina (Reanal, act. II) with benzene–ethanol (0—10%). Elution gave 143 mg (15%) of di-O-methyl derivative *VIII* (R_F 0·79, alumina, S_3), 245 mg (28·9%) of 2-O-methyl derivative *VI* (R_F 0·54), 115 mg (13·1%) of 3-O-methyl derivative *VII* (R_F 0·44) and 127 mg (15·7%) of the starting compound *V* of R_F 0·12.

Methyl 4,6-*dideoxy*-2-O-*methyl*-α-L-lyxo-*hexopyranoside* (VI), syrup boiling at 50°C/0·1 Torr (bath temperature), $[\alpha]_D^{23}$ −42·4 ± 0·6° (*c* 0·95, chloroform); PMR (measured in $(CD_3)_2CO$): H_1: 4·72 p.p.m., $J_{1,2}$ = 1·7 Hz; H_2: 3·17 p.p.m., $J_{2,1}$ = 1·7 Hz, $J_{2,3}$ = 3·5 Hz; H_3 and H_5: approx. 3·75 p.p.m. (complex multiplet); H_{4e}: 1·52 p.p.m., $J_{4e,3}$ = 5 Hz, $J_{4e,4a}$ = 13 Hz, $J_{4e,5}$ = = 2·5 Hz; H_{4a}: 1·45 p.p.m., $J_{4a,3}$ = 9·5 Hz, $J_{4a,4e}$ = 13 Hz, $J_{4a,5}$ = 9·5 Hz; H_6: 1·12 p.p.m., $J_{6,5}$ = 6·5 Hz; OCH_3: 3·30 and 3·43 p.p.m., OH (−70°C; 4·55 p.p.m., J_{OH,H_3} = 9 Hz. For $C_8H_{16}O_4$ (176·2) calculated: 54·53% C, 9·15% H; found: 54·69% C, 9·12% H.

Methyl 4,6-*dideoxy*-3-O-*methyl*-α-L-lyxo-*hexopyranoside* (VII), syrup boiling at 50°C (bath temperature) at 0·1 Torr, $[\alpha]_D^{24}$ −87·5 ± 2° (*c* 0·9, chloroform); PMR (measured in $(CD_3)_2CO$): H_1: 4·62 p.p.m., $J_{1,2}$ = 1·7 Hz; H_2: 3·79 p.p.m., $J_{2,1}$ = 1·7 Hz, $J_{2,3}$ = 3·5 Hz; H_3: 3·48 p.p.m., $J_{3,2}$ = 3·5 Hz, $J_{3,4e}$ = 6 Hz, $J_{3,4a}$ = 11 Hz; H_{4e}: 1·58 p.p.m., $J_{4e,3}$ = 6 Hz, $J_{4e,4a}$ = 13 Hz, $J_{4e,5}$ = 2·5 Hz; H_{4a}: 1·51 p.p.m., $J_{4a,3}$ = 11 Hz, $J_{4a,4e}$ = 13 Hz, $J_{4a,5}$ = 9 Hz; H_5: approx. 3·75 p.p.m. (multiplet); H_6: 1·16 p.p.m., $J_{6,5}$ = 6·5 Hz, OCH_3: 3·30 p.p.m., OH (−70°C): 4·40 p.p.m., J_{OH,H_2} = 5 Hz, For $C_8H_{16}O_4$ (176·2) calculated: 54·53% C, 9·15% H; found: 54·62% C, 9·40% H.

Methyl 4,6-*dideoxy*-2,3-*di*-O-*methyl*-α-L-lyxo-*hexopyranoside* (VIII), syrup, b.p. 30—40°C at 0·1 Torr, $[\alpha]_D^{22}$ −59·0 ± 1·5° (*c* 0·6, chloroform); PMR: H_1: 4·78 p.p.m., $J_{1,2}$ = 1·7 Hz; H_2:

3·42 p.p.m., $J_{2,1} = 1·7$ Hz, $J_{2,3} = 3·5$ Hz; H_3: 3·62 p.p.m.; H_{4e}: approx. 1·68 p.p.m.; H_{4a}: approx. 1·61 p.p.m.; H_5: approx. 3·75 p.p.m.; H_6: 1·23 p.p.m., $J_{6,5} = 6·5$ Hz; OCH_3: 3·55, 3·38 and 3·50 p.p.m.. For $C_9H_{18}O_4$ (190·2) calculated: 56·82% C, 9·53% H; found: 57·02% C, 9·56% H.

Preparative Gas Chromatography

A mixture of methyl ethers *II*, *III* and *IV* was separated at a preparative scale on a Fractovap GV apparatus (Carlo Erba, Italy), using a 200 × 1 cm column packed with Chromosorb W (30—60 mesh) impregnated with 5% of Carbowax 20 M. The flow rate of the carrier gass — helium — was 60 ml/min, column temperature 185°C, evaporator temp. 220°C. The separated mixture (12·55 g) was injected into the column in 100 µl portions in approx. 80% xylene solution. The yield of methyl ether *II* was 4·28 g, of methyl ether *III* 1·62 g, methyl ether *IV* 1·50 g, and the discharge weighed 5·16 g and was further worked up. The purity of the substances was controlled on a Chrom III apparatus (Laboratorní přístroje, Prague) using a column of 180 × 0·4 cm dimensions, filled with Silocel C 22 (AW — HMDS) and 5% of fixed Carbowax 20 M, at a 172°C temperature and carrier gas flow rate 20 ml/min of nitrogen.

4,6-Dideoxy-2-O-methyl-D-*xylo*-hexose (*IX*)

A solution of 1·68 g of glycoside *II* in 8 ml of 60% acetic acid was refluxed for 12 hours. After this period thin-layer chromatography showed no further change in the composition of the reaction mixture. After evaporation the syrupy residue was chromatographed on a column of 50 g silica gel. Elution with benzene–ethanol mixture gave 159 mg (9·5%) of the starting glycoside *II* and 1·323 mg (85%) of hexose *IX* which after crystallisation from an ether–hexane mixture had m.p. 59·5—61·5°C, $[\alpha]_D^{22}$ +86° (3 min.) → +63·0° (3 hours, constant, *c* 1·6, water). For $C_7H_{14}O_4$ (162·2) calculated: 51·84% C, 8·70% H; found: 51·79% C, 8·83% H.

4,6-Dideoxy-3-O-methyl-D-*xylo*-hexose (*X*)

Applying the above mentioned procedure hexose *X* was prepared from glycoside *III* in 81% yield. M.p. 90—92°C, $[\alpha]_D^{24}$ +133° (2 minutes) → +75·2° (3 hours, constant, *c* 1·3, water). Literature[5] gives for natural D-chalcose m.p. 91—93°C, $[\alpha]_D$ +120° → +76° (3 hours, water), or[6]: m.p. 93—94°C, $[\alpha]_D$ +121·5° (15 min. → +76·8° (*c* 4·1, water, 24 hours). For $C_7H_{14}O_4$ (162·2) calculated: 51·84% C, 8·70% H; found: 51·66% C, 8·68% H.

4,6-Dideoxy-2,3-di-O-methyl-D-*xylo*-hexose (*XI*)

Using the above method glycoside *IV* was transformed to hexose *XI* in 80% yield; syrup b.p. 84—90°C/0·01 Torr, $[\alpha]_D$ +92·5 ± 1° (*c* 0,9, water). For $C_8H_{16}O_4$ (176·2) calculated: 54·53% C, 9·15% H; found: 54·51% C, 9·36% H.

4,6-Dideoxy-2-O-methyl-L-*lyxo*-hexose (*XII*)

A solution of 141 mg of glycoside *VI* in 3 ml of 0·5N-H_2SO_4 was heated at 90°C for 2 hours. After cooling the mixture was neutralised by filtration through a 5 ml column of Amberlite 4-B (OH^-). The syrup obtained after evaporation of the eluate (131 mg) was purified by chromatography on 10 g of silica gel CH. The syrupy product was distilled at 100°C (bath temp.) and

0·02 Torr. Yield 85 mg (syrup), $[\alpha]_D^{26}$ +8·7° ± 2° (*c* 0·5, water). For $C_7H_{14}O_4$ (162·2) calculated: 51·84% C, 8·70% H; found: 51·52% C, 8·95% H.

4,6-Dideoxy-3-O-methyl-L-*lyxo*-hexose (*XIII*)

By an analogous procedure hexose *XIII* was prepared from glycoside *VII* in 91% yield, m.p 106–107°C (after sublimation *in vacuo* at 0·03 Torr and 100°C bath temperature), $[\alpha]_D^{22}$ +9·9 ± ± 1° (*c* 0·9, water). For $C_7H_{14}O_4$ (162·2) calculated: 51·84% C; 8·70% H; found: 52·04% C, 8·66% H.

4,6-Dideoxy-2,3-di-O-methyl-L-*lyxo*-hexose (*XIV*)

The same procedure applied to glycoside *VIII* gave syrupy hexose *XIV* in 76% yield, b.p. 70 to 80°C at 0·05 Torr, $[\alpha]_D^{24}$ +13·5 ± 2° (*c* 0·6, water). For $C_8H_{16}O_4$ (176·2) calculated: 54·53% C, 9·15% H; found: 54·80% C, 9·50% H.

The authors thank Mrs J. Červená for technical assistance during the preparation of the starting glycoside I, *Mr V. Ineman for the analysis of the prepared compounds by gas chromatography, Dr P. Trška, Dr V. Kubelka and Dr J. Mitera for the measurement of the PMR and mass spectra, and Mr J. Vaňura for his help during the work with Fractovap GV apparatus. Elemental analyses were carried out in the Department of organic analysis of the Central laboratories, Institute of Chemical Technology, Prague.*

REFERENCES

1. Lawton B. T., Szarek W. A., Jones J. K. N.: Carbohydrate Res. *14*, 255 (1970).
2. Kefurt K., Kefurtová Z., Jarý J.: This Journal *36*, 1701 (1971).
3. Kochetkov N. K., Wulfson N. S., Chizhov O. S., Zolotarev B. M.: Tetrahedron *19*, 2209 (1963).
4. Kochetkov N. K., Usov A. I.: Tetrahedron Letters *1963*, 519.
5. Woo P. W. K., Dion H. W., Bartz W. Q.: J. Am. Chem. Soc. *83*, 3352 (1961).
6. Keller-Schierlein W., Roncari G.: Helv. Chim. Acta *45*, 138 (1962).
7. Foster A. B., Stacey M., Webber J. M., Westwood J. H.: Proc. Chem. Soc. *1963*, 279.
8. McNally S., Overend W. G.: Chem. Ind. (London) *1964*, 2021.
9. Lawton B. T., Ward D. J., Szarek W. A., Jones J. K. N.: Can. J. Chem. *47*, 2899 (1969).
10. Srivastava R. M., Brown R. K.: Can. J. Chem. *48*, 830 (1970).
11. Belder A. N., Lindberg B., Theander O.: Acta Chem. Scand. *16*, 2005 (1962).
12. Garegg P. J.: Acta Chem. Scand. *17*, 1343 (1963).
13. Norrman B.: Acta Chem. Scand. *22*, 1381 (1968).
14. Norrman B.: Acta Chem. Scand. *22*, 1623 (1968).
15. Handa N., Montgomery R.: Carbohydrate Res. *11*, 467 (1969).
16. Owen L. N.: Chem. Commun. *1967*, 527.

Translated by Ž. Procházka.