Preliminary communication

Isolation of permethylated dicarbonyl sugar derivatives from polysaccharides[*]

N. KASHIMURA, KJ. YOSHIDA, and K. ONODERA

Laboratory of Biological Chemistry, Department of Agricultural Chemistry, Kyoto University Kyoto (Japan)

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Partially methylated monosaccharides have been converted into various types of derivatives for the purpose of linkage analysis of polysaccharides. Among the derivatives used are phenylazobenzoates[1], trimethylsilyl ethers[2], alditol acetates[3], and aldononitriles[4]. In view of recent progress in dicarbonyl sugar synthesis[5], the introduction of a carbonyl group followed by derivatisation seemed to offer an alternative procedure. We now report the isolation of three anomeric pairs of 2,4-dinitrophenylhydrazones of permethylated dicarbonyl monosaccharides isolated from cellulose, laminarin, and dextran.

Oxidation of methanolysates of permethylated polysaccharides with methyl sulphoxide oxidants produced anomeric mixtures of the corresponding dicarbonyl sugars which were converted into crystalline 2,4-dinitrophenylhydrazones. Separation of anomers of the hydrazones was performed by preparative thin-layer chromatography (Silica Gel G; benzene–ethyl acetate, 17:3).

Thus, cellulose gave methyl 2,3,6-tri-*O*-methyl-D-*xylo*-hexopyranosid-4-ulose 2,4-dinitrophenylhydrazone (**1**) in 70–80% yield[†]; α-anomer, m.p. 163°, $[\alpha]_D^{26}$ +85.7°, τ 4.96 (H-1, $J_{1,2}$ 3.7 Hz); β-anomer, m.p. 221°, $[\alpha]_D^{26}$ −77.0°, τ 5.50 (H-1, $J_{1,2}$ 7.0 Hz)[††]. Permethylated laminarin (from *Laminaria hyperborea*) gave methyl 2,4,6-tri-*O*-methyl-D-*ribo*-hexopyranosid-3-ulose 2,4-dinitrophenylhydrazone (**2**) in 80% yield; α-anomer, m.p. 227°, $[\alpha]_D^{17}$ +341°, τ 4.97 (H-1, $J_{1,2}$ 3.5 Hz); β-anomer, m.p. 213°, $[\alpha]_D^{17}$ +129°, τ 5.28 (H-1, $J_{1,2}$ 7.5 Hz). Methyl sulphoxide–phosphorus pentaoxide[6] was used for the above oxidations. Oxidation of anomeric mixtures of methyl 2,3,4-tri-*O*-methyl-D-gluco-

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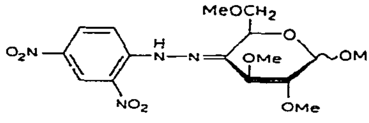
[†] Yields are based on anomeric mixtures of partially methylated methyl α- and β-D-glucosides.

[††] All crystalline compounds gave acceptable analyses. Melting points are uncorrected. Optical rotations (chloroform) were measured with a Yanagimoto direct-reading polarimeter. N.m.r. spectra ($CDCl_3$) were recorded with a Hitachi Perkin–Elmer R-20 spectrometer (90 MHz).

pyranoside derived from dextran was successfully performed with Me_2SO–dicyclohexylcarbodiimide[7] or Me_2SO–phosphorus pentaoxide[6] to yield methyl 2,3,4-tri-*O*-methyl-D-*gluco*-hexodialdo-1,5-pyranoside 2,4-dinitrophenylhydrazone (3) in 30–35% yield; α-anomer, m.p. 171°, $[\alpha]_D^{25}$ +56.2°, τ 5.14 (H-1, $J_{1,2}$ 3.2 Hz), τ 2.50 (H-6, $J_{5,6}$ 6.0 Hz); β-anomer, m.p. 169°, $[\alpha]_D^{25}$ ~0°, τ 5.70 (H-1, $J_{1,2}$ 7.2 Hz), τ 2.52 (H-6, $J_{5,6}$ 5.6 Hz).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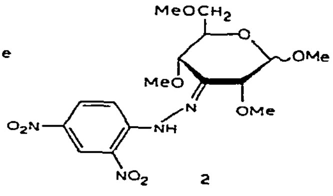
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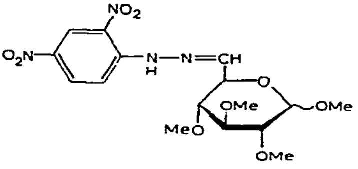
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The above derivatives showed different mobilities on t.l.c. (the same system as for p.l.c.). Investigation by mass spectrometry (Hitachi RMU-6 spectrometer and a Hitachi RMU-7 high-resolution spectrometer, operating at 70 eV) revealed further distinctive characteristics. Fig.1 shows the mass spectra of the β-anomers of compounds 1, 2, and 3. The respective pairs of α and β anomers gave similar spectra. The characteristic strong peaks at *m/e* 281.0495, 277.0534, and 266.0643 are assigned the elemental compositions $C_{10}H_9N_4O_6$, $C_{11}H_9N_4O_5$, and $C_{10}H_{10}N_4O_5$, respectively, and possible structures are shown in Fig.1.

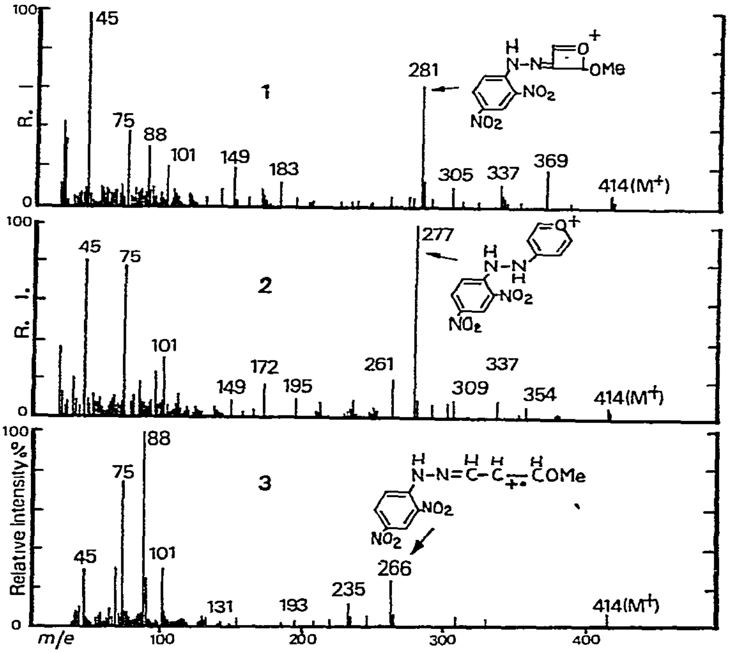

Fig.1. Mass spectra (70 eV) of the β-anomers of compounds 1, 2, and 3.

The preparation of other permethylated dicarbonyl sugar hydrazones, including oligosaccharide derivatives, is in progress.

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REFERENCES

1 G. H. Coleman, D. E. Rees, R. L. Sundberg and C. M. McCloskey, *J. Amer. Chem. Soc.*, 67 (1945) 381.
2 Y. C. Lee and C. E. Ballou, *Biochemistry*, 4 (1965) 257.
3 H. Björndal, B. Lindberg and S. Svensson, *Carbohyd. Res.*, 5 (1967) 433.
4 B. A. Dmitriev, L. V. Backinowsky, O. S. Chizhov, B. M. Zolotarev, and N. K. Kochetkov, *Carbohyd. Res.*, 19 (1971) 432.
5 B. F. Butterworth and S. Hanessian, *Synthesis*, (1971) 70; G. H. Jones and J. G. Moffatt, *Methods Carbohyd. Chem.*, 6 (1972) 314.
6 K. Onodera, S. Hirano and N. Kashimura, *Carbohyd. Res.*, 6 (1968) 276; J. H. Jordaan and S. S. Smedley, *Carbohyd. Res.*, 16 (1971) 177.
7 K. E. Pfitzner and J. G. Moffatt, *J. Amer. Chem. Soc.*, 87 (1965) 5661; D. H. Ball, F. H. Bisset, I. L. Klundt and L. Long, Jr., *Carbohyd. Res.*, 17 (1971) 165.