The Structure of Methyl α-D-Galacturonic Acid Methyl Ester

JOHAN HJORTÅS,[a] BJØRN LARSEN,[b] FRODE MO[a] and SRINUAN THANOMKUL[a]*

[a] Institutt for røntgenteknikk, Universitetet i Trondheim-NTH and [b] Institutt for marin biokjemi, Universitetet i Trondheim-NTH, N-7034 Trondheim-NTH, Norway

Uronic acids are constituents of a number of biologically important macromolecules. The physical and biological properties of these polymers are greatly influenced by the identity of the uronic acid, or acids, present and by conformational parameters for the uronic acid molecules. In contrast to other sugars such information is extremely scarce for the uronic acids. We have therefore initiated a program for the study of uronic acid conformation by X-ray crystallographic methods.

Methyl α-D-galacturonic acid methyl ester was synthesized according to the method of Jones and Stacey.[1] The yield was 20 % and the recrystallized product had a melting point of 148° C and $[\alpha]_D^{20} = 127°$ ($c = 1.0$, water.) Single crystals of suitable size were obtained by crystallization from a mixture of equal volumes of methanol and acetone at elevated temperatures.

Crystal data are: $C_6H_{14}O_7.H_2O$, orthorhombic space group $P2_12_12_1$, cell dimensions (with estimated standard deviations in parentheses) $a = 6.489(3)$ Å, $b = 8.004(3)$ Å, $c = 20.869(12)$ Å, calculated density 1.471 g cm^{-3} (measured 1.473 g cm^{-3}), number of molecules in the unit cell: $Z = 4$.

2386 observed reflexions were collected by an automatic Picker FACS-1 diffractometer using Mo$K\alpha$ radiation and the $\omega/2\theta$ scanning mode with max. $2\theta = 70°$. The structure was solved by a multisolution tangent refinement procedure using the program TANNY.[2] Refinement was performed by means of Fourier and least-squares techniques using programs from the XRAY system.[3] Refinement with isotropic temperature factors for all heavy atoms yielded the conventional R-factor of 0.060.

The pyranose ring has the expected $^4C_1$ chair conformation as shown in Fig. 1. The carbon atom C(8) of the glycosidic methyl group is *gauche* to the ring oxygen atom $O(5)$ and *trans* to C(2). The C(5) methyl ester group is nearly planar and equatorial to the ring, with $O(6)$ *cis* to O(5) and O(7) *trans* to O(5). The carboxyl C(6) – O(6) double bond is 1.190 Å, C(6) – O(7) is 1.326 Å and O(7) – C(7) is 1.443 Å. Other bond lengths and angles are similar to those of methyl α-D-galactopyranoside monohydrate[4] and other hexoses.[5]

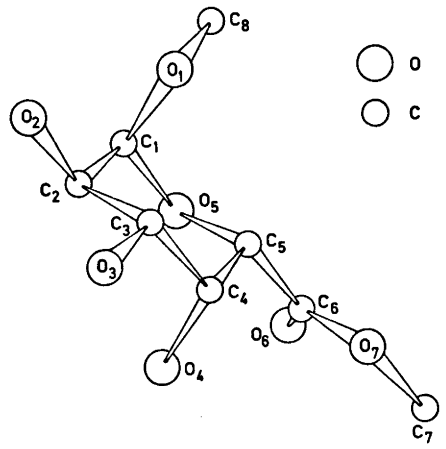

Fig. 1. Projection of the molecule, only with heavy atoms, on 100 plane.

Further refinement and a more detailed account of the structure will be published elsewhere. Additional work is in progress with the aim of obtaining information on the binding of cations to the uronic acids and their polymers. The results will also be valuable as basis for investigations of ionic bonds in solutions by other physical methods, *e.g.* NMR spectroscopy.

This work is part of S.T.'s thesis for a degree of Licentiatus Technicae (Lic. techn.) at The University in Trondheim-NTH sponsored by the Norwegian Agency for International Development (NORAD) which is gratefully acknowledged.

1. Jones, J.K.N. and Stacey, M. *J. Chem. Soc.* (1947) 1340.
2. Mo, F. *TANNY*, Report 17-RII-72, Institutt for røntgenteknikk, NTH (1972).
3. Stewart, J. M., Kruger, G. J., Ammon, H. L., Dickinson, C. and Hall, S. R. *The XRAY System*, Techn. report TR-192, Computer Science Center, Univ. of Maryland (1972).
4. Gatehouse, B. M. and Poppleton, B. J. *Acta Crystallogr. B 27* (1971) 654.
5. Arnott, S. and Scott, W. E. *J. Chem. Soc. Perkin Trans. 2* (1972) 324.

Received December 18, 1973.

* Permanent address: Physics Department, Faculty of Science, Chulalongkorn University, Bangkok 5, Thailand.