ACTA CHEMICA SCANDINAVICA 17 (1963) 1160–1188

Short Communications

The Structure of Anomeric Sugars : A Remark

SVEN FURBERG

Institute of Chemistry, University of Oslo, Blindern-Oslo

and

BJÖRN PEDERSEN

Central Institute for Industrial Research, Blindern-Oslo, Norway

In a number of papers published in this journal Blom [1-3] and Christiansen [4] have discussed several properties of anomeric sugars. They conclude that these properties can only be explained in a rational way if current assignment of structures to the α- and β-anomers is reversed. In the case of glucose, for example, this implies that α-glucose is the anomer having the all-equatorial arrangement of the hydroxyl groups.

For several reasons it is difficult to correlate properties and structure in sugar chemistry and it is desirable to confirm the structures by direct methods. Such confirmation has been given during the last fifteen years by X-ray crystal structure analysis of a considerable number of sugars, amongst these α-glucose [5], β-glucose [6], α-glucose monohydrate [7] and cellobiose [8], to quote only some investigations directly related to glucose. In each case the complete crystal structure has been derived and satisfactorily refined. We should like to add that the crystal structure of β-glucose independently has been determined also by us, using sign relationship methods (unpublished work). Any one of these investigations alone conclusively show that the current assignment is correct, α-glucose having the structure 1a2e3e4e5e, β-glucose the all-equatorial structure 1e2e3e4e5e. All structures considered together the evidence is overwhelming.

In solution direct evidence for the correctness of this assignment is furnished by proton magnetic resonance. Fig. 1 shows the high resolution NMR-spectrum of an equilibrium mixture of α- and β-glucose in slightly acidified heavy water solution at room temperature. The spectrum was recorded on a Varian asc. Dual Purpose Spectrometer operating at 60 Mc/sec. The two doublets designated α and β originates from the single proton directly attached to C_1. The labelling was determined from the spectrum of pure α- and β-glucose in the same solvents, and the relative intensities of the signals α and

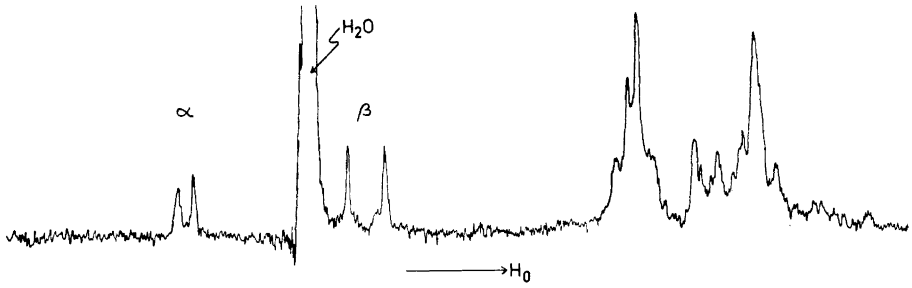

Fig. 1. The high resolution proton magnetic resonance spectrum of the equilibrium mixture of α- and β-glucose.

β are as expected from the known composition of the equilibrium mixture.

C_1 is the only carbon atom in the molecule which is linked to *two* oxygen atoms. The proton at C_1, H_1, is therefore shifted away from the band where the rest of the carbon-linked protons contribute. The β-doublet is shifted to 0.58 ppm at high field relative to the α-doublet. It is generally accepted that an axial proton will absorb at about 0.50 ppm higher field than its equatorial counterpart [9]. Hence, the bond C_1-H_1 is axial in β-glucose and equatorial in α-glucose, in accordance with the assignment.

The signal from H_1 is split to a doublet due to the spin-spin coupling with the proton at C_2. The β-doublet separation is measured to 7c/sec and the α-doublet splitting to 3c/sec. It is well known that the proton arrangement *aa* gives a larger splitting than *ea* (about 8c/sec for *aa* and 3c/sec for *ea*) [9]. Thus the magnitude of splitting also shows that the current assignment is correct.

The spectra of the unsubstituted anomers discussed in the present paper are in good agreement with results obtained for the pentaacetates dissolved in chloroform [10].

In conclusion, the structures of the anomers of glucose have been established beyond doubt in the solid state and in aqueous solution by direct physical methods. The structures of a number of other sugars have also been determined by these methods. Attempts, therefore, to explain the properties of sugars should take the results of these investigations into account.

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Received February 26, 1963.

Constituents of the Umbelliferous Plants

I. Constituents of the Root of *Angelica archangelica* L.

BENT EICHSTEDT NIELSEN
and HELMER KOFOD

Chemical Laboratory B, The Royal Danish School of Pharmacy, Copenhagen, Denmark

The original aim of the present work was to investigate the distribution of lignans in the plant family Umbelliferae. The investigation was prompted by the isolation of desoxypodophyllotoxin from *Anthriscus silvestris* L. [1] and from *Cicuta maculata* L. [2].

So far we have only been able to detect desoxypodophyllotoxin in Danish material of *Anthriscus* while the other Umbelliferae investigated do not seem to contain lignans.

The analytical method was the paper-chromatographic procedure previously described by one of us [3].

During the work we have isolated 15 different substances which are not lignans and we found it worth-while to focus our interest on these constituents.

In the present paper preliminary results from the work on *Angelica archangelica* L. are to be discussed.

The identity of the plant material (commercial drug) was established by microscopic comparison with autentic material. (*Angelica archangelica* L. subspecies *eu-archangelica* Thell., varietas *sativa* (Mill.) Rikle).

A new substance, $C_{49}H_{88}O_2$, m.p. 77.5°, considered to be *β-sitosteryl arachinate*, was obtained. The root also afforded β-sitosteryl palmitate, which has not previously been isolated from the family Umbelliferae. Furthermore, angelic acid, palmitic acid and behenic acid were obtained.

Exptration. Percolation with diethyl ether of *Angelica* root (5000 g) afforded 12 l of extract. The extract was concentrated to a volume of about $\frac{3}{4}$ l and stored at −10°. After 8 days of standing a pale yellow precipitate (P) was formed and collected on a filter.

The mother liquor was worked up according to Hata and Nitta [4]. The obtained fractions A, B and C were examined separately.