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Short Communications

Constitution of Resin Phenols and their Biogenetic Relations

XX *. The Identity of Pseudocubebin and *d*-Sesamin

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Recently fagarol was found to be identical with *dl*-sesamin [1]. In this paper pseudocubebin the last of the long known lignans of unsettled structure is proved to be *d*-sesamin (*cf.* Erdtman [2]).

In 1896 Peinemann [3] isolated a crystalline colourless substance (m. p. 122°) from the fruits of *Piper Lowong* Bl. From his analyses he calculated the formula $C_{20}H_{20}O_6$ which is the same as that for cubebin which had been isolated 60 years earlier from *Piper cubeba*. Peinemann showed that his substance was different from cubebin and he proposed the name pseudocubebin for the new compound.

Later Halberkann [4] found that pseudocubebin also occurred in the bark of *Ocotea usambarensis* Engl., Ibean Camphor tree, which occurs in East Africa, and on comparison of this substance with Peinemann's original preparation he showed that they were identical.

On oxidation with permanganate Peinemann obtained piperonylic acid. Attempted hydrolysis, transesterification and benzoylation invariably yielded unchanged starting material. Bromination afforded a dibromoderivative melting at 180° and nitration a substance giving the analytical figures for a dinitroderivative although no melting point was reported. From Peinemann's and Halberkann's results it appeared to be likely that pseudocubebin is a lignan most closely resembling sesamin.

Bark of *Ocotea usambarensis* was very kindly put at our disposal by Mr. B. G. Gilchrist, Lushoto Tanganyika.

The isolation of pseudocubebin was carried out mainly according to Halberkann. He reported a yield of about 0.5 % of pseudocubebin but our sample contained much less. The preparation melted at 122—123°, undepressed on admixture with authentic *d*-sesamin. The specific rotation was +64.5° (Halberkann gives +61°) and for *d*-sesamin the highest reported value is +69°. The series of colours developed when the compound was dissolved in sulphuric acid was identical with that for sesamin and also agreed with that given by Halberkann. Further the dibromoderivative of pseudocubebin was found to be identical with dibromo-*d*-sesamin as shown by melting point and mixed melting point determinations. Hence the "pseudocubebin" of *Ocotea usambarensis* is identical with *d*-sesamin.

Experimental. (All melting points uncorrected.) *Isolation of pseudocubebin.* The ground bark of *Ocotea usambarensis* (500 g) was exhaustively extracted with ether. The extract was distilled with steam and the non-volatile portion dissolved in ether and shaken with sodium hydroxide solution (2 N). The ether was evaporated and the oily residue dissolved in petroleum ether. After some time hard crystals (100 mg) deposited at the wall and bottom of the vessel. They were recrystallised from ethanol giving a colourless substance, m. p. 122—123°, $[\alpha]_D^{20}$ + 64.5° (*c* 1.75 in chloroform). The melting point was undepressed on admixture with an authentic sample of *d*-sesamin.

Dibromopseudocubebin. Pseudocubebin was brominated with bromine in chloroform. Crystallisation from ethanol gave very thin

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needles, m. p. 180—181°, mixed m. p. with dibromo-*d*-sesamin 181—183°.

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X-Ray Crystallographic Data on some Nucleic Acid Components

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X-Ray crystal structure analysis of decomposition products of nucleic acids may be expected to give valuable information on the structure of the macromolecule. The four nucleosides from RNA have earlier been studied by one of us [1]. In this paper the results of a preliminary investigation of some other nucleic acid components are reported.

Weissenberg and oscillation photographs were taken, using Cu$K\alpha$ and Fe$K\alpha$ radiation. Unit cell dimensions and space groups were derived and densities measured by the flotation method. The values given are believed to be accurate to within 1 %.

Crystals of thymine, D-ribose, 2-deoxy-D-ribose, deoxycytidine hydrochloride and thymidine were examined with the following result:

Thymine. Crystals grown from alcohol are needleshaped, elongated along b, with {100} prominent, whereas from water parallelepipeds are obtained, with all faces about equally developed. Both types of crystals are monoclinic with cell dimensions a = 12.87 Å, b = 6.83 Å, c = 6.72 Å and β = 105°. The density was found to be 1.46 g/cm³ and there are four (calculated 3.97) molecules in the unit cell. The only systematic absences occur in the $h0l$ reflections for l odd and in the $0k0$ reflections for k odd. The space group is therefore $P2_1/c$.

D-*Ribose.* Recrystallisation from a number of solvents yielded extremely small crystals, or syrups. From the melt, however, crystals big enough for X-ray work were grown at about 60° C. They had the shape of needles and were elongated along c. The diagrams showed them to be monoclinic twins with (100) as twin-plane. The twinning was difficult to detect, as the cell dimensions happen to be such that the reflections from the two twinned crystals very nearly coincide. The cell dimensions are: a = 6.57 Å, b = 21.59 Å, c = 4.80 Å and β = 113°. The density was found to be 1.59 g/cm³, corresponding to four molecules in the unit cell. The calculated density is also 1.59 g/cm³. The space group is $P2_1$.

Although a great number of simple sugars have been investigated by X-ray crystallographic methods by Cox *et al.*[2], and others, we have found no crystal data on ribose or 2-deoxy-ribose in the literature.

*2-Deoxy-*D-*ribose.* From the melt very thin flakes were obtained, with {100} prominent. The X-ray diagrams were rather poor; however, they showed that the crystals probably are orthorhombic, with a = 11.36 Å, b = 10.65 Å and c = 4.91 Å. The absences indicate the space group $P2_12_12_1$. Four molecules $C_5H_{10}O_4$ per unit cell gives a calculated density of 1.50 g/cm³.

Thymidine. This nucleoside crystallises in well-developed orthorhombic prisms elongated along c, with a = 16.27 Å, b = 13.86 Å and c = 4.86 Å. Four molecules per unit cell corresponds to a density of 1.47 g/cm³. Reflections $h00$ and $0k0$ are absent for odd values of h and k respectively. The $00l$ reflections were not all recorded, but as 001 and 003 appear to be absent, the space group is probably $P2_12_12_1$.

Deoxycytidine hydrochloride. Thin, monoclinic needles elongated along c, with a = 7.03 Å, b = 17.70 Å, c = 5.15 Å and β = 117°. Space group $P2_1$. Two mole-