

Molecular Conformation of 4- and 5-Hydroxypipelic Acids

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Two hydroxypipelic acids were isolated from *Rhapis*, *Acacia*, and *Albizia* species, as well as from some other plants, and characterized chemically by Virtanen and Kari as 5- and 4-hydroxypipelic acids^{1,2}. The position of the hydroxy group was estimated by oxidation with potassium permanganate whereby mainly, or only, glutamic acid was formed from the 5-hydroxy acid and aspartic acid beside other products, but no glutamic acid was formed from the 4-hydroxy acid.

Since doubts had been expressed regarding the position of the hydroxy group in the compound characterized as 4-hydroxypipelic acid³, the acid was reinvestigated thoroughly. The position of the hydroxy group was confirmed to be consistent with our previous result⁴.

The NMR spectra of 4- and 5-hydroxypipelic acids were obtained in the Varian Laboratories from preparations sent by one of us as early as in 1959. The mole-

cular conformation of these acids was hereby established. The estimation was repeated this year using an HR-100 High Resolution NMR Spectrometer operating at 100 mc/sec. The samples were dissolved in D₂O which resulted in a strong HDO peak in the spectrum due to exchange of the labile hydrogens. This peak was arbitrarily labelled zero and an audio-frequency sideband was introduced 350 cps upfield to serve as a calibration.

Fig. 1 shows the spectrum of 4-hydroxypipelic acid. The quintet at 52 cps must arise from H₁ since only this proton has four neighbors. Since all four are equally spin coupled to H₁, H₁ must be equatorial. The pair of doublets at 83 cps is assigned to H₂ since only this proton has just two neighbors. The large coupling, characteristic of axial-axial neighbors, shows that H₂ is axial. The pattern centered at 145 cps is assigned to H₃ and H₄ while the complex group of lines at higher field strengths are due to the remaining four protons. The structure and conformation shown in Fig. 3a is consistent with the NMR data.

Fig. 2 shows the spectrum of 5-hydroxypipelic acid. The resonance from H₁ at 102 cps is now a septet which must arise from coupling to two neighbors with a small coupling constant and coupling to two other neighbors with a coupling constant twice as large. The large coupling shows that H₁ is now axial. H₂ is also axial since it is strongly coupled according to the assignments of Fig. 2. Thus, the conforma-

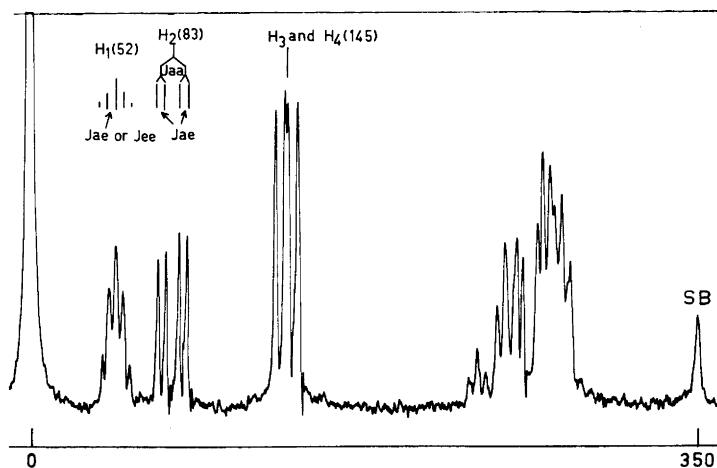


Fig. 1. The NMR-spectrum of 4-hydroxypipelic acid.

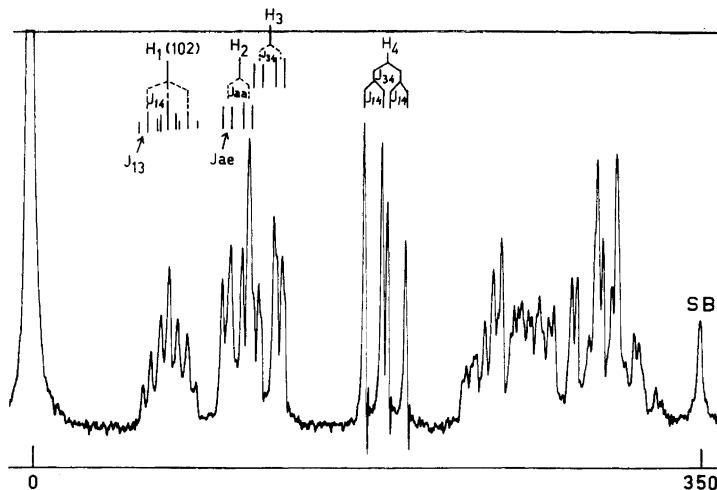
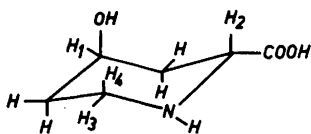
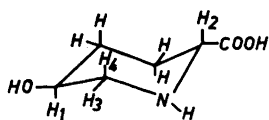


Fig. 2. The NMR-spectrum of 5-hydroxy-pipecolic acid.



a



b

Fig. 3. Molecular conformation of 4-hydroxy-pipecolic acid (a) and 5-hydroxy-pipecolic acid (b).

tion of Fig. 3b is consistent with the NMR data for 5-hydroxy-pipecolic acid.

Witkop and Foltz⁵ estimated the configuration of 5-hydroxy-pipecolic acid, and Clark-Lewis and Mortimer⁶ that of 4-hydroxy-pipecolic acid using a chemical method. Their result is in agreement with ours.

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On the Existence of the Suboxides Cr_3O and Mo_3O

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In two papers published in 1954 Schönberg reported the preparation of two new oxides of chromium and molybdenum with the probable formulas Cr_3O ¹ and Mo_3O ². Neither was obtained as a single phase.

Cr_3O was said to be formed by three different methods, namely (a) when Cr_2O_3 was reduced with titanium, vanadium or zirconium at about 1500°C, (b) when chromium metal was oxidized by steam in a large excess of hydrogen at 600°C, and (c) in trace amounts when chromium metal