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ACID CATALYZED HYDRATION OF 3-DEHYDRO-GIBBERELLIN A_3; PARTIAL SYNTHESIS OF 1ß-HYDROXYLATED GIBBERELLIN A_1 AND PSEUDO GIBBERELLIN A_1

G. Adam * and Ph. D. Hung

Institute for Plant Biochemistry

of the Research Centre for Molecular Biology and Medicine, Academy of

Sciences of the G.D.R., Halle (Saale), German Democratic Republic

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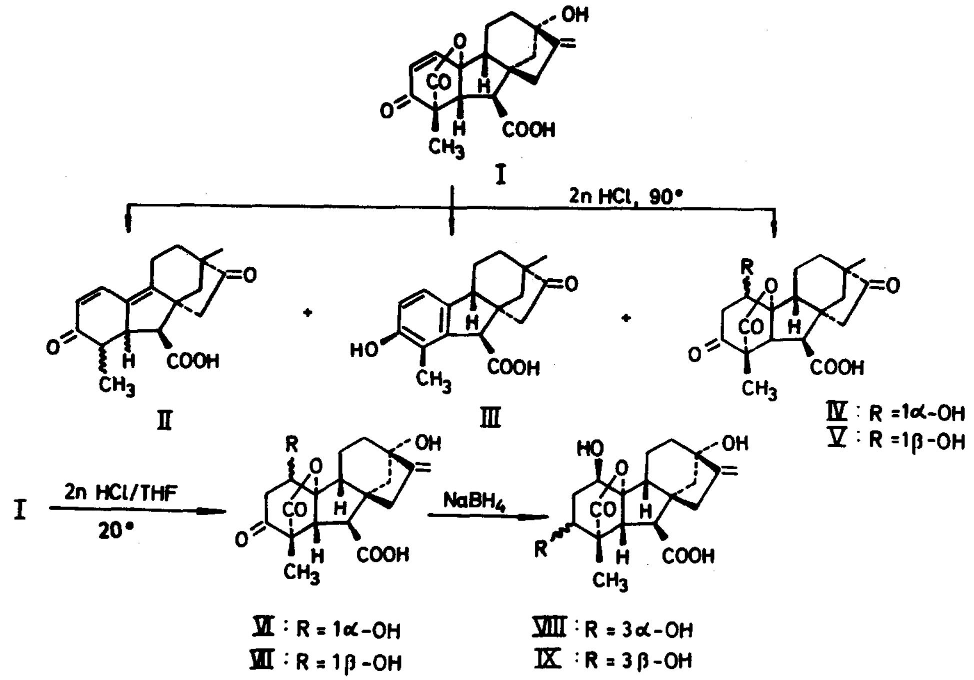
We wish to report on our results concerning the acid catalyzed hydration of 3-dehydro GA_3 I (1). Thus, reaction of I with 2N HCl (4 hrs. at 90°C) affordes the compounds II-V separable by repeated SiO_2 chromatography. The main product (53%) was the dienone acid II (m.p. 144°C, $[\alpha]_D^{23}$ +74.5° in ethanol) resulting from decarboxylation and Wagner-Meerwein-rearrangement of I; M^+ 300 m/e; IR: ν_{max}^{nujol} 1575, 1620, 1660 (dienone), 1735 (5 membered carbonyl), 3400 cm^{-1} (hydroxyl); UV: $\lambda_{max}^{methanol}$ 215, 307 nm (10 200, 21 500); 60 MHz NMR: $\delta_{TMS}^{aceton-d_6}$ 1.03 (s, 17-H_3), 1.06 (d, J=6Hz, 18-H_3), 2.48 (dd, J=9Hz, J'=6Hz, 5-H), 2.97 (d, J=9 Hz, 6-H), 5.94 (d, J= 10Hz, 2-H), 7.45 ppm (d, J= 10Hz, 1-H). The known (2) oxophenolic acid III was isolated (21%) as a second product arising from decarboxylation and skeleton rearrangement. The two other compounds have been identified as 1-epimeric hydroxydioxo acids IV (m.p. 265-8°C (dec.), $[\alpha]_D^{23}$+102.7°, 10%) and V (m.p. 257-60°C (dec.), $[\alpha]_D^{23}$ +84.7°, 15%) on the basis of their mass spectra (M^+ 362 m/e) and other physical data. The configuration at the newly created asymmetric C-1 is indicated by the coupling pattern of the 1-methine protons in the 100 MHz NMR spectra (3) (X-part of ABX-system) with $J_{AX}+J_{BX}\approx 15$ Hz for compound IV and 7 Hz for the 1ß-epimer V at 4.36 and 4.50 ppm, respectively, as well as by the molecular amplitudes of the carbonyl Cotton effects with a= +72 and +97 for IV and V. Reaction of I with 2N HCl/THF (5:3^{v}/v) at 20°C for 120 hrs. gave the 1-hydroxy-3-oxo gibberellins VI (m.p.215°C (dec.), $[\alpha]_D^{23}$+97.2°, 8%) and VII (m.p. 235-8°C (dec.), $[\alpha]_D^{20}$+98.5°, 62%) with M^+ 362 m/e besides 21% of the rearranged 1ß-hydroxy dioxo acid V. Subsequent Wagner-Meerwein-rearrangement with trifluoro acetic acid for 50 hrs. at 20°C transforms VI and VII to the corresponding hydroxydioxo acids IV and V, respectively. $NaBH_4$ reduction



of VII (0.5 hrs. in methanol) followed by repeated SiO_2 chromatography afforded 1β-hydroxy GA_1 IX (m.p. 245-7°C (dec.), $[\alpha]_D^{25}$+41.0°) as well as 1β-hydroxy pseudo-GA_1 VIII (m.p. 153°C, $[\alpha]_D^{25}$+21.0°) in a 3:1 ratio (M^+ 364 m/e). Their stereochemistry at C-3 is confirmed by NMR data; whereas the 5-proton doublet in VIII appears at 3.12 (J=10Hz) the corresponding signal of the epimeric IX was found 0.68 ppm downfield by virtue of 1.3-diaxial deshielding of the 5-proton, indicating β-orientation of the 3-hydroxy group in the latter case.

References

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3) E.P.Serebryakov, N.S.Kobrina, V.F.Kucherov, G.Adam and K.Schreiber, Tetrahedron 28, 3819 (1972).