FORMATION OF 1-DEOXY-1-(INDOLYL-3)-α-L-SORBOPYRANOSES AND THEIR N-ALKYL DERIVATIVES FROM ASCORBIGINE AND N-ALKYLASCORBIGINES

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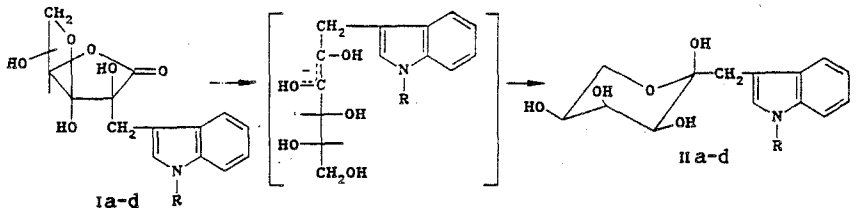
Ascorbigine, 2-C[(indolyl-3)methyl]-β-L-threo-L-glycero-3-hexulofuranoso-1,4-lactone (Ia), which is an ascorbic acid derivative contained in plants, undergoes cleavage of the lactone ring, decarboxylation, and rearrangement upon treatment with base (pH 11-12, 20°C, 12 h), resulting in the formation of amorphous 1-deoxy-1-(indolyl-3-)-α-L-sorbopyranose (IIa) in 30% yield. An analogous conversion takes place with the previously synthesized [1, 2] N-substituted ascorbigines Ib-d. Sorbopyranoses IIa-d were purified by chromatography on silica gel using a chloroform–methanol, 8:1, eluent system.



Ia-d R

IIa-d

I, II a R=H; b R=CH_3; c R=$CH_2CH=CH_2$; d R=C_4H_9

"Rapid atom bombardment" (RAB) (utilizing Xe) mass spectrometry of these compounds revealed the following m/e values for their protonated molecular ions: 280 (IIa), 294 (IIb), 320 (IIc), and 336 (IIId).

The hydrocarbon regions in the PMR spectra of these compounds (IIa-d) are very similar both with respect to signal position and the splitting patterns of the signals to the spectra of α-L-sorbopyranoses III (with a $^2C_5$ conformation). This confirms the presence of a similar molecular fragment in compounds IIa-d. The upfield shift of the 3-H and 5a-H ($\Delta\delta$ = 0.2 ppm), with retention of the signal positions of the 4-H and 6a-H atoms, relative to compound III, is indicative of an axial orientation of the hydroxyl group attached to C(2). It would appear, therefore, that the L-sorbopyranoses IIa-d exist in a $^2C_5$ conformation with an α-configuration at the anomeric carbon.

α-L-Sorbopyranose (III). PMR spectrum (C_5D_5N): 4.63 (1H, t, $J_{34} = J_{45}$ = 9.0 Hz, 4-H); 4.47 (1H, t, $J_{6a5} = J_{6a6e}$ = 10.3 Hz, 6-H_a); 4.38 (1H, d, $J_{11'}$ = 11.0 Hz, 1-H); 4.35 (1H, d, 3-H); 4.25 (1H, d, 1'-H); 4.23 (1H, m, 5-H); 4.16 ppm (1H, dd, J_{6e5} = 5.6 Hz, 6e-H).

α-L-Sorbopyranose (IId). PMR spectrum (C_5D_5N): 4.60 (1H, t, $J_{43} = J_{45}$ = 9.0 Hz, 4-H); 4.44 (1H, t, $J_{6a5} = J_{6a6e}$ = 9.1 Hz, 6-aH); 4.13 (1H, dd, J_{6e5} = 5.6 Hz, 6e-H); 4.07 (1H, d, 3-H); 4.04 (1H, m, 5-H); 3.90 (1H, d, $J_{11'}$ = 13.9 Hz, 1-H); 3.75 ppm (1H, d, 1'-H).

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