

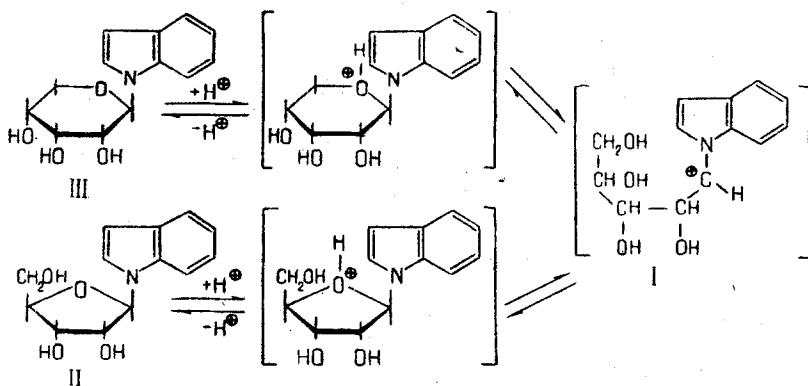
GLYCOSYLINDOLES

VIII. Isomerization of the Carbohydrate Ring of 1-Ribosylindoles

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Khimiya Prirodnykh Soedinenii, Vol. 4, No. 2, pp. 128-129, 1968

It has previously been shown that under the conditions of the detritylation reaction (boiling with 80% acetic acid), 1-(D- β -5'-O-trityl-2', 3'-di-O-acetylribosylfuranosyl)indole forms, in addition to 1-(D- β -2', 3'-di-O-acetylribofuranosyl)indole, a small amount of the corresponding ribopyranose derivative, giving 1-(D- β -ribopyranosyl)indole after deacetylation [1]. The isomerization of the carbohydrate ring can be explained by the formation of the noncyclic carbocation (I), which is an intermediate link in the chain of interconversions of 1-(D- β -ribofuranosyl)indole and 1-(D- β -ribopyranosyl)indole (III) and their derivatives.



It might be expected that 1-(D-ribopyranosyl)indole (III) would isomerize into 1-(D- β -ribofuranosyl)indole (II) under the action of acids. In fact, when III was boiled with 80% acetic acid, II was formed with a yield of 6.6%. The substance was identified chromatographically and from its IR spectrum. Similar results were obtained when III was boiled with 0.2% and also with 2% sulfuric acid, but the yield of II was only 4.0%. Simultaneously with isomerization, in all cases hydrolysis took place as was shown by the formation of indole.

The scheme for the isomerization of the carbohydrate ring does not exclude the possibility of simultaneous anomeration and the formation of α -pyranosides and α -furanosides. However, when III is isomerized into II no formation of the α -anomers has been detected, which can be explained by the presence of configurational hindrance.

So far as we know, there is no information in the literature on the isomerization of the carbohydrate rings of nucleosides and their analogs. A number of examples of interconversions of derivatives of alkyl ribopyranosides and alkyl ribofuranosides has been described [2, 3].

Experimental

With heating, 0.3 g of 1-(D- β -ribopyranosyl)indole was dissolved in 10 ml of 80% acetic acid, the solution was boiled for 15 min, and the acetic acid was distilled off in vacuum, finally with the addition of absolute methanol. The residue was dissolved in a mixture of acetone and water (7 : 1) and deposited on an Al_2O_3 column (l 40 cm, d 20 mm). It was eluted with a mixture of acetone and water (7 : 1). Indole was eluted in the first fractions, followed by 1-(D- β -ribopyranosyl)indole, and the last fractions contained 1-(D- β -ribofuranosyl)indole. The yield of II was 0.02 g (6.6%). The fractions were investigated by chromatography in a thin layer of Al_2O_3 in the acetone-water (7 : 1) system. R_f of indole 1.0; R_f of III 0.82; R_f of II 0.12. The 1-(D- β -ribofuranosyl)indole obtained was identical with an authentic sample [1] in respect of its IR spectrum and the results of paper chromatography [paper treated with borate buffer, pH 8.7, in the 1-butanol-pyridine-water (6 : 4 : 3) system, R_f 0.73].

Summary

It has been shown that 1-(D- β -ribopyranosyl)indole isomerizes under the action of acids to form 1-(D- β -ribofuranosyl)indole.

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13 March 1967

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