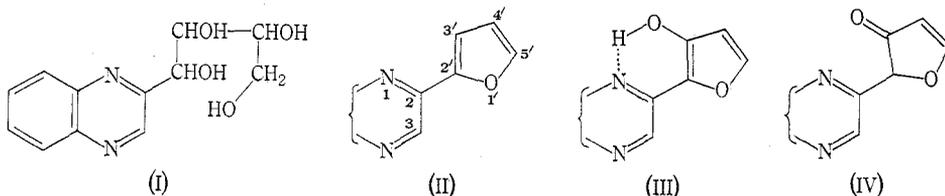


THE STRUCTURE OF 2-(3-HYDROXYFUR-2-YL)QUINOXALINE*

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The action of strong sulphuric acid on 2-(D-arabino-tetrahydroxybutyl)-quinoxaline (I) is to dehydrate and cyclize the side chain to give 2-fur-2'-yl-quinoxaline (II). This product, first isolated by Maurer and Schiedt,¹ was given its correct structure and synthesized by Gomez-Sanchez and co-workers.² These latter workers³ also assigned the structure (III), 2-(3-hydroxyfur-2-yl)quinoxaline, to a small amount of an enolic by-product formed at the same time and evidently the result of dehydrogenation as well as dehydration. Evidence for this structure was based upon ultraviolet and infrared spectra and upon its conversion to (II) by heating with zinc dust. Recently however, this structure has been questioned.⁴



The n.m.r. spectrum of the compound has now been measured and confirms structure (III). The reason for placing the hydroxyl group at C3' rather than at C4' had been because, in that position, it could most readily form an intramolecular hydrogen bond with one of the nitrogen atoms. The n.m.r. spectrum of compound (III) confirms this location. The entire lack of a peak in the same spectrum for a methine hydrogen shows the absence of any of the tautomeric 3'-keto-compound (IV). This is in keeping with the fact that where hydrogen bonding can occur, as it has been shown for example in 2-acetyl-3-hydroxyfuran,⁴ the compound can exist as a 3-hydroxyfuran; otherwise the compound is converted completely into the furan-3-one.

The n.m.r. spectrum of (III) shows a pair of doublets (δ 6.38† and δ 7.37, $J_{4'5'}$ 2.0 c/s) which are assigned to the 4' and 5' protons respectively. Had the substituent been in the 4' position then the longer-range splitting constant $J_{3'5'}$

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‡ Relative to Me₄Si as internal reference (δ 0.00) in CDCl₃ solution.

¹ Maurer, K., and Schiedt, B., *Ber. dt. chem. Ges.*, 1934, **67**, 1980; Maurer, K., Schiedt, B., and Schroeter, H., *Ber. dt. chem. Ges.*, 1935, **68**, 1717.

² Gomez-Sanchez, A., Yruela-Antinolo, M., and Garcia Gonzalez, F., *An. R. Soc. Esp. Fis. Quim.* B, 1954, **50**, 431.

³ Gomez-Sanchez, A., and Yruela-Antinolo, M., *An. R. Soc. Esp. Fis. Quim.* B, 1955, **51**, 1955.

⁴ Rosenkranz, R. E., Allner, K., Good, R., Phillipsborn, W., and Eugster, C. H., *Helv. Chim. Acta*, 1963, **46**, 1259.

would have been⁵ about 1.0 c/s. The enolic proton with a value δ 8.7 was quickly exchanged upon addition of deuterium oxide. With respect to these three protons the spectrum corresponds closely to that of 2-acetyl-3-hydroxyfuran.⁴

The spectrum of (II) shows the expected quadruplet, δ 6.68 ($J_{3'4'}$ 3.5 c/s; $J_{4'5'}$ 2.0 c/s) for the 4'-proton and a doublet at δ 7.4 ($J_{3'4'}$ 3.5 c/s) for the 3'-proton. The signal for the 5'-proton falls within the multiplet associated with the quinoxaline moiety but it can be assigned a value approximately δ 7.7. The value for the 3-proton of the quinoxaline ring did not change significantly between compound (II) (δ 9.17) and compound (III) (δ 9.11).

⁵ Gronowitz, S., Sorlin, G., Gestblom, B., and Hoffman, R. A., *Ark. Kemi*, 1962, **19**, 483.