immediately before measurements, because the dissolved anils underwent more than 50% hydrolysis on several days standing in this medium.

pH *of the solutions* was measured by means of a PHM 4c apparatus (Radiometer, Copenhagen) and a glass electrode type B of the same firm (correction for the salt error only over pH 11·5).

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NUCLEIC ACID COMPONENTS AND THEIR ANALOGUES. CXLIV.*
SYNTHESIS OF 5¹,5²-AZINODI(2-β-D-RIBOFURANOSYL-*as*-TRIAZIN-3(4*H*)-ONE)

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The reaction of 5-chloro-2-(2,3,5-tri-O-acetyl-β-D-ribofuranosyl)-*as*-triazin-3(2*H*)-one[1] (*V*) and hydrazine in benzene–methanol affords a yellow substance the elemental analysis and molecular weight of which is in accordance with the formula $C_{28}H_{34}N_8O_{16}$. Deacetylation with methanolic ammonia leads to the parent nucleoside $C_{16}H_{22}N_8O_{10}$ the ultraviolet spectrum of which in acidic and neutral media exhibits a significant maximum at 350—351 nm; in alkali, the spectrum shows a bathochromic shift of the maximum to 388 nm. From the theoretically possible tautomeric structures of this nucleoside, both lactam forms are the most probable, namely, the azino form *I* and the hydrazo form *II*. The infrared spectrum of the chloroform-soluble acetyl derivative shows a single band of the stretching vibration of the free NH group at 3360 cm^{-1}. The wavenumber of this band corresponds well to the $N_{(4)}$—H triazine group situated between two exocyclic double bonds. Thus under analogous conditions, the ν(NH) band is situated at 3374 cm^{-1} with 1-methyl-6-azauracil[2] and at 3 363 cm^{-1} with 1-methyl-4-thio-6-azauracil[2]. It is noteworthy that the ν(NH) band of hydrazobenzene (solution in chloroform) as model of the form *II* is also situated in this region (3380 cm^{-1} and shoulder at 3 330 cm^{-1}).

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The triazinone carbonyl ν(C=O) band of the acetyl derivative in chloroform (1 713 cm^{-1}) lies at considerably high values and indicates the presence of a NH group in the α-position. The known infrared spectra of 1-methyl-6-azacytosine (*III*) and 3-methyl-6-azacytosine[3] (*IV*) may also be used in determination of the tautomeric structure of the above yellow substance. Thus, Table I clearly indicates the spectral similarity of the acetyl derivative *VI* and compound *IV* possessing an exocyclic C=N bond in the region of double bond stretching vibrations. Consequently, the acetyl derivative is ascribed the azine structure *VI* and the structure *VII* belongs to the parent nucleoside.

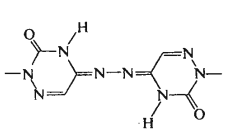
TABLE I

Wavenumbers (cm^{-1}) in Dimethyl Sulfoxide

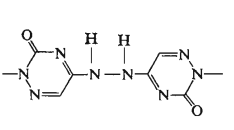
Compound	ν(C=O)	ν(C=N)
III	1 666 sh [a], 1 645 [b]	1 605, 1 586, 1 526
IV	1 706, 1 658 sh	1 626 [b], 1 591
VI	1 708 [b]	1 640, 1 585

[a] Shoulder; [b] the most intensive band in the "carbonyl" region.

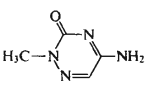
As indicated by π-electron energy calculation of a simplified model by the Hückel LCAO–MO method, the azine tautomeric form is energetically more advantageous, the total π-electron energy E_π of 5[1],5[2]-azinodi(2-methyl-1,2,4-triazin-3(4*H*)-one) being 33·4834β and that of 1,2-di(2-methyl-2,3-dihydro-3-oxo-1,2,4-triazinyl)hydrazine being 33·0133β. Compound *VII* is stable towards air-oxidation even in alkali in contrast to the recently reported 6,6-bisadenine[4]. In the latter case, the presence of a hydrazo system is indicated by the ready oxidation to the azo deriva-



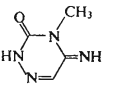
I



II

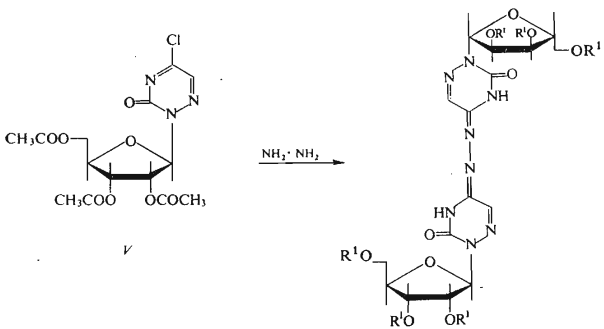


III



IV

tive. Formation of the acetyl derivative *VI* is analogous to the reaction of 2-iodo-1-methylquinolinium iodide with hydrazine where the proton shift results in stabilization to the azine[5] Compound *VII* does not inhibit the growth of *Escherichia coli* (inorganic medium, glucose) at the concentration of 1000 μg per 1 ml.



V

VI, $R^1 = COCH_3$
VII, $R^1 = H$

EXPERIMENTAL

Ultraviolet spectra were taken on a Beckman DU type apparatus. Infrared spectra were recorded on a Zeiss UR-10 spectrophotometer. Quantum calculations were performed on an Elliot 503 computer (standard program for Hückel LCAO-MO,* Autocode 503 Mk.4, parameters according to ref.[6,7]). The η value equal to 0·9 was used for the N—N hydrazine group.

$5^1,5^2$-Azinodi(2-(2,3,5-tri-O-acetyl)-β-D-ribofuranosyl-*as*-triazin-3(4*H*)-one) (*VI*)

A solution of the chloro derivative *V* (crude materal, prepared from 5 mmol of 2′,3′,5′-tri-O-acetyl-6-azauridine according to ref.[1]) in a mixture of benzene (12 ml) and chloroform (20 ml) is cooled down to −60°C and treated dropwise under stirring with a solution of 80% hydrazine hydrate (0·17 ml) and triethylamine (0·7 ml) in methanol (5 ml). The cooling is then interrupted and the reaction mixture is stirred at room temperature for 20 hours. The precipitate of triethylamine hydrochloride is filtered off, the filtrate evaporated to dryness, and the crystalline residue recrystallised from methanol (100 ml) to afford 720 mg of the yellow substance *VI*, m.p. 129 to 130°C. Concentration of mother liquors afforded additional 220 mg, m.p. 125—128°C. The analytical sample melted at 130—131°C (methanol). Ultraviolet spectrum (80% aqueous ethanol): λ_{max} 243 nm, λ_{max} 353—356 nm, λ_{min} 278 nm. For $C_{28}H_{34}N_8O_{16}$ (738·6) calculated: 45·45% C, 4·56% H, 15·15% N; found: 45·13% C, 4·78% H, 14·98% N. Without triethylamine, the analogous reaction gave a lower (half) yield.

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$5^1,5^2$-Azinodi(2-β-D-ribofuranosyl-*as*-triazin-3(4*H*)-one) (*VII*)

A solution of the acetate *VI* (200 mg) in 30% methanolic ammonia (10 ml) was allowed to stand at room temperature for 20 hours, evaporated, and the crystalline residue triturated with methanol (3 ml) to afford 110 mg (83%) of the nucleoside *VII*, m.p. 259—260°C. The analytical sample melted at 260°C (30% aqueous methanol). For $C_{16}H_{22}N_8O_{10}$ (486·4) calculated: 39·68% C, 4·55% H, 23·05% N; found: 39·69% C, 4·74% H, 22·80% N. Paper chromatography, R_F value: at the start line in 1-butanol–water (85 : 15) and 0·21 in 2-propanol–concentrated aqueous ammonia–water (7 : 1 : 2). Ultraviolet spectrum, pH 1: λ_{max} 239 nm (ε 12·3 . 10^3), λ_{max} 351 nm (ε 25·6 . 10^3), λ_{min} 278 nm (ε 4·3 . 10^3); pH 7: λ_{max} 237 nm (ε 13·1 . 10^3), λ_{max} 350 nm (ε 24·0 . 10^3), λ_{min} 278 nm (ε 4·75 . 10^3); pH 13: λ_{max} 252 nm (ε 12·0 . 10^3), λ_{max} 388 nm (ε 21·2 . 10^3), λ_{min} 309 nm (ε 6·1 . 10^3).

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NUCLEIC ACID COMPONENTS AND THEIR ANALOGUES. CXLV.* N-SUBSTITUTION OF URACIL AND 5-BROMOOROTIC ACID

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As reported in an earlier paper[1] of this Series, the reaction of 6-azauracil and benzyl chloride in aqueous sodium hydroxide has furnished 1-benzyl-6-azauracil. Under analogous conditions, uracil (*I*) and benzyl chloride afford 1-benzyluracil (*II*). The structure of compound *II* was established by cyanoethylation to compound *II* which was identical with the specimen obtained by benzylation of 3-(2-cyanoethyl)uracil[2,3] (*IV*). Consequently, the course of benzylation

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