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Original Scientific Paper

Hydropyrimidines. V. Isomeric Dihydro 2- and 4-Oxopyrimidines

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Desulfurization of thio analogs of 5,6-dihydrouracil and partial hydrogenation of oxypyrimidines* were investigated as synthetic routes for the preparation of isomeric dihydropyrimidines.

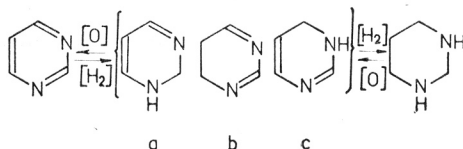
The synthesis of unstable 1-methyl-5,6-dihydro-4-oxopyrimidine (IX) from 1-methyl-5,6-dihydro-2-thiouracil (X) is described. Desulfurization of 5,6-dihydro-2-thiouracil (XV) and its 3-methyl derivative (XI) afforded the corresponding dihydro-4-oxo-pyrimidines XVI and XII having the double bond at $\Delta^{1,2}$ position. The structures of XII and XVI were confirmed by hydrogenation to the tetrahydro compounds XVII and XIII.

The more stable dihydro-2-oxopyrimidines III, IV and XIX were prepared from the corresponding 4-thiouracils XX, XXI and XVIII.

The NMR spectra of 2- and 4-oxopyrimidines, their dihydro and tetrahydro derivatives as well as of 5,6-dihydrouracil and its thio analogs are discussed.

The recent determination of the complete nucleotide sequence of an alanine transfer ribonucleic acid (RNA)¹ revealed *inter alia* the presence of 5,6-dihydrouridylic acid as the nucleotide residue.² The first report of the natural occurrence of dihydropyrimidines in a nucleic acid confirmed our earlier assumption³⁻⁵ that the dihydropyrimidines could be incorporated into RNA.

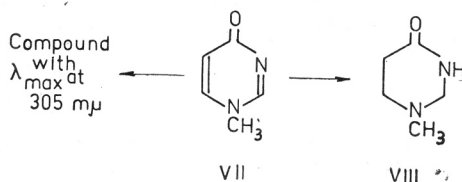
Tetrahydropyrimidines⁶ were first prepared by Skinner and Wunz⁷ but informations concerning the synthesis and stereochemistry of dihydropyrimidines are scarce. Thus, no data have been reported in the literature of possible effects related to the position of double bonds in heterocyclic rings *a*, *b* and *c* or about the behavior of these isomeric compounds in oxidation-reduction processes. Additional data regarding the conformation of dihydropyrimidines and its nonbonded interactions, when incorporated in the polyribonucleotide chains, could probably clarify possible imperfections in base pairing.



* The substituted pyrimidines are named without regard to keto-enol tautomerism, *i. e.* the nomenclature does not reflect the actual state of the molecule.

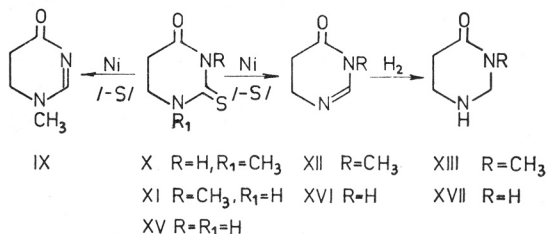
In this paper we wish to report about the synthesis and chemical properties of hitherto unknown isomeric dihydro 2- and 4-oxypyrimidines. For this purpose the partial hydrogenation of substituted pyrimidines as well as the desulfurization of thio analogs of 5,6-dihydrouracil were explored as possible synthetic routes.

In a previous paper⁴ we reported that the catalytic hydrogenation of 2-hydroxypyrimidine (I) and its *N*-methyl derivative (II) offers a selective route to 3,6-dihydro-2-hydroxypyrimidines III and IV. However, the attempt to prepare dihydroderivatives of 4-oxypyrimidine (V) and its 3-methyl derivative VI failed. The exhaustive hydrogenation of 1-methyl-4-oxypyrimidine⁸ (VII) resulted in the formation of 1-methyl-1,2,5,6-tetrahydro-4-oxypyrimidine (VIII). The partial hydrogenation of VII yielded a compound showing an unexpectedly high absorption at 305 m μ .



We found the desulfurization of thio analogs of 5,6-dihydrouracil and its methyl derivatives (with Raney nickel) to the corresponding hydroxypyrimidines as a reaction of considerable preparative significance. To avoid the conversion of the thiocarbonyl group into methylene group a catalyst deactivated by boiling with acetone was used. The instability of the so obtained hydroxypyrimidines was the main obstacle in the isolation and purification of these compounds.

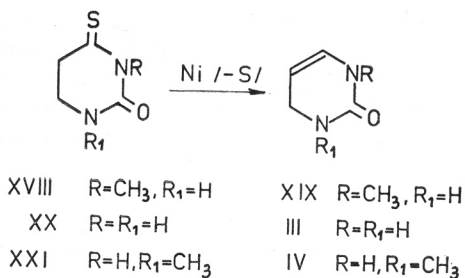
Compound IX tentatively identified as 1-methyl-5,6-dihydro-4-oxypyrimidine was prepared from 1-methyl-5,6-dihydro-2-thiouracil⁵ (X). It could not be isolated because of its instability. Compound IX with double bond at $\Delta^{2,3}$ position shows in UV an absorption band at 269 m μ which disappears in protic solvents. This is most probably due to the formation of the *N*-formyl derivative of 3-methylaminopropionamide. We hope to ascertain the course to this ring opening in a forthcoming investigation.



The removal of sulfur from 3-methyl-5,6-dihydro-2-thiouracil⁵ (XI) afforded 3-methyl-5,6-dihydro-4-oxypyrimidine (XII) with the double bond at $\Delta^{1,2}$ position. The structure of XII was proved by hydrogenation and conversion of the thus obtained tetrahydro derivative XIII into 3-methyl-1-nitroso-1,2,5,6-tetrahydro-4-oxypyrimidine (XIV).

The desulfurization of 5,6-dihydro-2-thiouracil³ (XV) yielded 5,6-dihydro-4-oxypyrimidine (XVI) having an absorption band at 226 m μ , log ϵ 3.804 and the double bond situated at $\Delta^{1,2}$ position. The position of the double bond was deduced from the similarity of the UV absorption spectrum with the spectrum of XII (λ_{\max} 239.5 m μ , log ϵ 3.700). Compound IX having a double bond at $\Delta^{2,5}$ position absorbs at higher wavelengths λ_{\max} 269 m μ , log ϵ 3.371). 1,2,5,6-Tetrahydro-4-hydroxypyrimidine (XVII) obtained by reduction of XVI was identical with a sample prepared by catalytic hydrogenation of 4-hydroxypyrimidine⁴ (V).

The preparation of dihydropyrimidines from 4-thio analogs of 5,6-dihydro-uracil proceeds in higher yields than from 2-thio analogs. This is probably due to the more stable dihydro 2-oxo structure. Thus the Raney nickel desulfurization of 3-methyl-5,6-dihydro-4-thiouracil (XVIII) yields undoubtedly 3-methyl-1,6-dihydro-2-oxypyrimidine (XIX). When 5,6-dihydro-4-thiouracil (XX) and 1-methyl-5,6-dihydro-4-thiouracil (XXI) are treated in the same way the possibility exists for a concurrent 3,4 and 4,5 double bond formation. However, only 3,6-dihydro-2-hydroxypyrimidine (III) and 1-methyl-3,6-dihydro-2-hydroxypyrimidine (IV) respectively were obtained which were previously prepared from 2-hydroxypyrimidine (I) and 1-methyl-2-hydroxypyrimidine⁴ (II).



The NMR spectral characteristics of 2-hydroxypyrimidine (I), its methyl derivative (II) and the corresponding 3,6-dihydro- (III, IV) and 3,4,5,6-tetrahydropyrimidines (XXII, XXIII) are listed in Table I. The chemical shifts and coupling constants confirmed the structure of these compounds. The *N*-methyl group influences the general pattern of pyrimidine spectra. Thus, I showed the signals related to AB₂ pattern indicating the predominance of the symmetrical hydroxy form. However, in the *N*-methylated compound II the chemical shifts protons in 4,5 and 6 position are different and the spectrum is of an ABC type. As expected the *N*-methyl group of hydroxypyrimidines has a negligible effect upon the chemical shifts of the ring protons, but the spectrum changes markedly in altering the dihydro into tetrahydro structure. Additional information about dihydropyrimidines III and IV were given earlier.⁴

The spectra of 4-oxypyrimidine (V), its 3-methyl derivative (VI), the corresponding 5,6-dihydro- (XVI, XII) and 1,2,5,6-tetrahydropyrimidines (XVII, XIII) presented in Table II are the least informative among all examined 2-oxypyrimidines. For tetrahydro derivatives the protons in position 2 give rise to resonance in the τ 5.7—5.92 region. No resonance for protons in the 2-position was observed in the spectrum of the dihydro compounds XVI and XII when

TABLE I
 Results from NMR Measurements of 2-Oxopyrimidines

Compound	Chemical shifts, τ				coupling const.		
	4-H	5-H	6-H	CH ₃	$J_{4,5}$	$J_{5,6}$	$J_{4,6}$
I	1.54 (2)	3.22 (3)	1.54 (2)	—	5.5	5.5	
	1.67	3.60	1.67	—	5.3	5.3*	
II	1.32 (4)	3.27 (4)	1.78 (4)	6.36	6.5	6.5	1.8
III [†]	3.82 (6)	5.08 (6)	5.95 (4)	—	8.0	3.5	1.8
IV [†]	3.83 (6)	5.08 (6)	5.95 (4)	7.08	8.0	3.5	2.5
XXII	6.76 (3)	8.19 (5)	6.76 (3)	—	6.0	6.0	
XXIII	6.62 (3)	8.00 (5)	6.66 (3)	7.06	6.0	6.0	

Figures in brackets denote the number of line of multiplets. Spin coupling constants J are given in c. p. s. (see Tables I and II).

* In acetone⁹

taken in deuterium oxide. The lack of this band indicates either the fast exchange of this proton by deuterium or a ring opening to the *N*-formyl derivative. The appearance of a signal at τ values 1.8 when XVI and XII were allowed to stand for a while in the same solvent supports the hypothesis of a ring rupture. Further investigations of these interesting solvent effects are planned.

 TABLE II
 Results from NMR Measurements of 4-Oxopyrimidines

Compound	Chemical shifts, τ				Coupling const.		
	2-H	5-H	6-H	CH ₃	$J_{5,6}$	$J_{2,5}$	$J_{2,6}$
V	1.53 (3)	3.43 (4)	1.92 (4)	—	6.8	1.2	0.8
	0.57 (3)	2.93 (2)	1.77 (4)	—	7.8		1.6*
	1.83	3.71	2.14		6.75	1.05	0.7**
VI	1.52	3.39 (2)	1.93 (2)	6.40	6.6		
XVI		7.40 (3)	6.40 (3)	—	6.5		
XII		7.38 (3)	6.37 (3)	7.05	6.7		
XVII	5.80	7.65 (3)	6.95 (3)	—	6.4		
XIII	5.70	7.54 (3)	6.83 (3)	7.13	6.3		
DHU	—	7.33	6.54	—	6.9	—	—
XV	—	7.03	6.16	—	7.0	—	—*
X	—	7.15	6.22	6.52	7.0	—	—*
XI	—	7.14	6.42	6.44	7.0	—	—*

* In trifluoroacetic acid (20% solution)

** In dimethylsulfoxide⁹

Finally, the NMR spectra of 5,6-dihydrouracil (DHU) was recorded and was found to be similar to those of 5,6-dihydro-2-thiouracil (XV) and its 1-methyl- (X) and 3-methyl derivative (XI) (Table II). Because of insolubility the spectra of XV, X and XI could not be recorded in deuterium oxide.

EXPERIMENTAL

Melting points, uncorrected, were taken on a Kofler hot stage. The UV spectra were measured in 95% ethanol on a Perkin-Elmer model 137 UV spectrophotometer with automatic gain control. The IR absorption bands were recorded in potassium bromide plates on a Perkin-Elmer Infracord 137 spectrophotometer and reported in wavelengths followed by relative intensities in brackets. The NMR spectra were taken at a frequency of 60 mC/sec. on a Varian Model A 60 high resolution spectrometer. Solutions (8–10%) in deuterium oxide, unless otherwise stated, were used. The sweep was calibrated using the common modulation sideband method. Values given for the chemical shifts are in part per million, tetramethylsilane taken as zero.

1,2,5,6-Tetrahydro-1-methyl-4-oxopyrimidine (VIII)

1-Methyl-4-oxopyrimidine (XII, 55 mg., 0.5 mmole) prepared from 1-methyl-2-methylthio-4-oxopyrimidine according to the procedure of Brown,⁸ was dissolved in anhydrous methanol (2.5 ml.) and 10 per cent of palladium on carbon catalyst (20 mg.) was added. The mixture was hydrogenated under pressure of 45 psi. at room temperature for 90 minutes. The catalyst was filtered off and the filtrate evaporated to an oil which crystallized on standing. It was distilled at $90^{\circ}/4 \cdot 10^{-2}$ mm. Yield 40 mg. (71%). A resublimed analytical sample melted at 61 – 63° .

Anal. $C_5H_{10}N_2O$ (114.15) calc'd.: C 52.61; H 8.83; N 24.54%
found: C 52.64; H 9.12; N 24.74%

IR-spectrum: 3.12 (s), 3.45 (s), 3.65 (s), 6.12 (s), 6.85 (s), 7.12 (m), 7.18 (m), 7.35 (s), 7.60 (s), 7.72 (s), 7.85 (s), 8.35 (m), 8.90 (s), 10.35 (m), 10.53 (m), 12.40 (m), 13.95 (w) μ .

Partial Hydrogenation of 1-Methyl-4-oxopyrimidine

1-Methyl-4-oxopyrimidine⁸ (VII, 110 mg., 1 mmole) in anhydrous methanol (6 ml.) was hydrogenated over 10 per cent palladium on carbon until one equivalent has been consumed (about 15 minutes). The oily product dissolved in dioxane was chromatographed on silica gel and eluted with dioxane (75 ml.). The eluate on evaporation yielded 52 mg. of a crystalline component with m.p. 95 – 105° . It was sublimed at $135^{\circ}/4 \cdot 10^{-2}$ mm.; 20 mg., m.p. 116 – 118° .

UV-spectrum: λ_{\max} 222 m μ , $\log \epsilon$ 3.88; 305 m μ , $\log \epsilon$ 3.88; λ_{\min} 257 m μ , $\log \epsilon$ 2.70.
IR-spectrum: 3.15 (m), 3.35 (m), 3.70 (w), 6.25 (s), 6.77 (s), 7.16 (s), 7.53 (m), 8.07 (s), 8.40 (s), 9.89 (w), 12.60 (s) μ .

Desulfurization of 5,6-Dihydro-2-thiouracils with Raney Nickel

General procedure. — W-2 Raney nickel was prepared by the method of Mzingo.¹⁰ Water was decanted and replaced by acetone. This suspension was refluxed and stirred for 2 hours. It was assumed that 1 ml. of the settled suspension contained equivalent to 0.6 g. of nickel.

To a warm anhydrous dioxane solution of 5,6-dihydro-2-thiouracil and its N-methyl derivatives in a nitrogen atmosphere (in dark) Raney nickel, previously washed with dioxane, was added and the mixture refluxed. The catalyst was filtered off and the filtrate evaporated to dryness under reduced pressure. The purification procedure and the physical constants of the respective products are given below.

1-Methyl-5,6-dihydro-4-oxopyrimidine (IX). — 1-Methyl-5,6-dihydro-2-thiouracil⁵ (X, 150 mg., 1.04 mmole) in dioxane (20 ml.) was treated with Raney nickel (2.1 ml.) for 30 minutes. The residue, a hygroscopic oil, distilled at $135^{\circ}/4 \cdot 10^{-2}$ mm. (unstable on air and in protic solvents). Yield 30 mg. (26%).

UV-spectrum: λ_{\max} 207 m μ , $\infty \log \epsilon$ 3.6; 269 m μ , $\infty \log \epsilon$ 3.3; λ_{\min} 238 m μ , $\infty \log \epsilon$ 2.7.

3-Methyl-5,6-dihydro-4-oxopyrimidine (XII). — 3-Methyl-5,6-dihydro-2-thiouracil⁵ (XI, 300 mg., 2.08 mmole) in dioxane (30 ml.) was refluxed for 10 minutes in the presence of Raney nickel (4.2 ml.). An oily precipitate separated from dioxane-hexane

which crystallized on standing, m. p. 56–63°. Yield 116 mg. (50%). (Yield 52% on the basis of spectroscopic data). For analysis it was sublimed at $40^{\circ}/3 \cdot 10^{-2}$ mm. and then crystallized from benzene-hexane, m. p. 63–65°. The spectrum of the compound changed when it was dissolved in protic solvents or exposed to air.

Anal. $C_5H_8N_2O$ (112.13) calc'd.: C 53.55; H 7.19; N 24.99%
found: C 53.70; H 7.00; N 25.22%

UV-spectrum: λ_{\max} 239.5 m μ , log ϵ 3.80. IR-spectrum: 2.90 (w), 3.45 (w), 6.01 (s), 6.12 (s), 7.25 (m), 7.40 (s), 7.78 (s), 8.20 (m), 9.70 (s), 10.08 (m), 11.50 (s) μ .

5,6-Dihydro-4-oxopyrimidine (XVI). — 5,6-Dihydro-2-thiouracil³ (XV, 500 mg., 3.85 mmole) in dioxane (50 ml.) was treated with Raney nickel (8 ml.) and refluxed for 10 minutes. The solution was concentrated to a volume of 10 ml. and purified by adding hexane. The precipitated impurities were filtered off and the filtrate evaporated to an oil (245 mg.), immediately sublimed at $100^{\circ}/4 \cdot 10^{-2}$ mm. Yield 100 mg. (27%), 33% based upon spectroscopic data, m. p. 133–135°. Recrystallized from dioxane-hexane, colorless prisms, yielded 75 mg. (20%), m. p. 137–138°.

Anal. $C_4H_6N_2O$ (98.10) calc'd.: C 48.97; H 6.17; N 28.56%
found: C 49.20; H 6.38; N 28.51%

UV-spectrum: λ_{\max} 226 m μ , log ϵ 3.80. IR-spectrum: 3.13 (m), 3.28 (m), 3.56 (m), 5.90 (s), 5.96 (s), 6.12 (s), 6.68 (w), 7.22 (m), 7.38 (m), 7.95 (s), 8.23 (m), 8.55 (m), 9.98 (m), 11.18 (s) μ .

3-Methyl-1,2,5,6-tetrahydro-4-oxopyrimidine (XIII)

3-Methyl-5,6-dihydro-4-oxopyrimidine (XII, 65 mg., 0.58 mmole) in anhydrous methanol (7 ml.) was hydrogenated over 5% rhodium on carbon under a pressure of 70 psi. for 3 hours. The separated oil, 62 mg., was distilled at $65^{\circ}/3 \cdot 10^{-2}$ mm. Yield 35 mg. (53%). The same tetrahydro derivative³ was obtained from 3-methyl-4-oxopyrimidine (VI). IR spectra of both samples were superimposable.

3-Methyl-1-nitroso-1,2,5,6-tetrahydro-4-oxopyrimidine (XIV)

3-Methyl-1,2,5,6-tetrahydro-4-oxopyrimidine (XIII, 26.5 mg., 0.23 mmole) in water (1 ml.) and acetic acid (0.05 ml.) was treated with sodium nitrite as described for de-methyl derivative.⁴ Yield 31.5 mg. (96%). For analysis it was distilled at $85^{\circ}/3 \cdot 10^{-2}$ mm.

Anal. $C_5H_9N_3O_2$ (143.15) calc'd.: C 41.95; H 6.34%
found: C 42.05; H 6.20%

IR-spectrum: 2.99 (w), 3.50 (w), 6.05 (s), 6.79 (m), 7.03 (s), 7.22 (m), 7.52 (s), 7.64 (s), 7.94 (m), 8.34 (m), 9.19 (s), 9.62 (w), 9.81 (w), 10.30 (w), 13.02 (w) μ .

1,2,5,6-Tetrahydro-4-oxopyrimidine (XVII)

5,6-Dihydro-4-oxopyrimidine (XVI, 20 mg.) in anhydrous methanol (1 ml.) was hydrogenated over 5% rhodium on carbon under pressure of 600 psi. for 6 hours. The tetrahydro derivative XVII, melted at 90–91°, undepressed on admixture with an authentic sample³ obtained from 4-oxopyrimidine. IR spectra of both samples were superimposable.

Desulfurization of 5,6-Dihydro-4-thiouracils with Raney Nickel

The desulfurizations were performed under the same condition as described for 2-thio analogs.

3-Methyl-1,6-dihydro-2-oxopyrimidine (XIX). — 3-Methyl-5,6-dihydro-4-thiouracil⁵ (XVIII, 115 mg., 0.8 mmole) in dioxane (12 ml.) was refluxed for 20 minutes in the presence of Raney nickel (1.8 ml.). The clear solution was concentrated to 1 ml. and applied to a chromatographic plate coated with 20 g. of silica gel (Merck, as described earlier⁵). The development was carried out with *n*-butanol by the ascending method. The fraction with $R_f \approx 0.5$ detected by a UV₂₅₄ lamp was removed mechanically from the plate and then eluted with anhydrous methanol. Yield 33 mg. (37%)

and 77% based upon spectroscopic data, m. p. 98—102°. For analysis it was sublimed at $85^{\circ}/4 \cdot 10^{-2}$ mm., m. p. 101—102°.

Anal. $C_5H_8N_2O$ (112.13) calc'd.: C 53.55; H 7.19; N 24.99%
found: C 53.39; H 7.42; N 24.97%

UV-spectrum: λ_{\max} 207.5 m μ , log ϵ 3.30; 255 m μ , log ϵ 3.39; λ_{\min} 225 m μ , log ϵ 3.032.
IR-spectrum: 3.15 (m), 3.29 (m), 3.49 (m), 3.71 (m), 6.05 (s), 6.13 (s), 6.81 (s), 7.19 (m), 7.88 (s), 9.19 (m), 10.03 (m), 13.11 (m) μ .

1-Methyl-3,6-dihydro-2-oxopyrimidine (IV). — 1-Methyl-5,6-dihydro-4-thiouracil⁵ (XXI, 124 mg., 0.86 mmole) dissolved in dioxane (12 ml.) was treated with Raney nickel (1.9 ml.) for 20 minutes. The filtered solution was concentrated to 1 ml. and separated using a chromatographic plate as described for compound XIX. The fraction with $R_f \sim 0.5$ was removed mechanically and eluted with anhydrous methanol. Yield 19 mg. (20%) and 55% based on spectroscopic data, m. p. 119—121° undepressed on admixture with a sample obtained by partial hydrogenation of 1-methyl-2-oxopyrimidine.¹ IR and UV spectra of both samples were superimposable.

3,6-Dihydro-2-oxopyrimidine (III). — 5,6-Dihydro-4-thiouracil⁵ (XX, 110 mg., 0.85 mmole) purified on a silica gel column by elution with methylene chloride was dissolved in dioxane (11 ml.) and treated with Raney nickel (1.6 ml.) for 30 minutes. The clear solution was concentrated to 1 ml. and separated on a chromatographic plate as described for compound XIX. The fraction with $R_f \sim 0.5$ was eluted with anhydrous ethanol. Yield 20 mg., m. p. 145° (extended). It was purified by passing through a silica gel column. The elution with methylene chloride-ethyl acetate (2:1) afforded a pure sample, m. p. 157—158° undepressed on admixture with a sample obtained from 2-oxopyrimidine.¹ IR and UV spectra of both samples were superimposable.

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IZVOD

Hidropirimidini. V. Izomerni dihidro 2- i 4-oksopirimidini

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Ispitani su sintetski putevi desulfuriranja tio analogona 5,6-dihidrouracila kao i parcijalno hidriranje oksopirimidina u svrhu priprave izomernih dihidropirimidina.

Opisana je sinteza nestabilnog 1-metil-5,6-dihidro-4-oksopirimidina (IX) iz 1-metil-5,6-dihidro-2-tiouracila (X). Desulfuriranje 5,6-dihidro-2-tiouracila (XV) i njegovog 3-metil derivata (XI) daje odgovarajuće dihidro-4-oksopirimidine XVI i XVII

sa dvostrukim vezom u poziciji $\Lambda^{1,2}$. Strukture XII i XVI su potvrđene njihovim hidriranjem do tetrahidro spojeva XVII i XIII.

Stabilniji dihidro 2-oksopirimidini III, IV i XIX su priređeni iz odgovarajućih 4-tiouracila XX, XXI i XVIII.

Obrađeni su NMR spektri 2- i 4-oksopirimidina, njihovih dihidro- i tetrahidro derivata kao i 5,6-dihidrouracila i njegovih tio analogona. Infracrveni i ultraljubičasti spektri opisanih tvari su zabilježeni u detaljima.

INSTITUT »RUĐER BOŠKOVIĆ«
ZAGREB

Primljeno 27. studenog 1965