line material separates from the boiling solvent. This material has been identified as a mixture of nucleosides, all of which appear to have not previously been reported. One of them was readily obtained by repeated recrystallization from water in form of clear needles of a high degree of purity. It melted at 246–247°; $[\alpha]^{22}$D +80.0° (c, 1.1 in 8% sodium hydroxide), and $[\alpha]^{22}$D +92° (c, 0.88 in pyridine). Anal. Calcd. for $C_{10}H_{14}N_2O_6$: C, 46.50; H, 5.48; N, 10.85. Found: C, 46.84; H, 5.42; N, 11.09. In neutral aqueous solution, the absorption spectrum showed a single maximum at 2690 Å. (E_M 9,250). The failure of this compound to show a spectral response to a change in the pH is similar to that described in the case of thymine desoxyriboside.[2]

Vigorous hydrolysis of the nucleoside with boiling 10% sulfuric acid afforded thymine, m. p. 321°. Anal. Calcd. for $C_5H_6N_2O_2$: C, 47.62; H, 4.79; N, 22.21. Found: C, 47.29; H, 4.15; N, 22.09. Its absorption spectra determined in neutral and basic media were identical with those of an authentic sample of thymine. As yet the conventional methods for the isolation and identification of the carbohydrate fragment of the nucleoside have been unsuccessful. The following evidence, however, proves the compound to by a thymine pentofuranoside. Upon benzoylation by means of a modified Schotten-Baumann method a tribenzoate was obtained, m. p. 190–191°; $[\alpha]^{22}$D +78.3° (c, 0.28 in methanol). The tri-p-bromobenzoate similarly prepared melted at 223–224°. Anal. Calcd. for $C_{31}H_{23}O_9N_2Br_3$: Br, 29.70. Found: Br, 28.74. Titration of the nucleoside according to the method of Lythgoe and Todd[3] consumed one mole of periodate without the formation of formic acid. The high dextrorotatory power of the nucleoside suggests that it is a xylofuranoside rather than the as yet unknown thymine ribofuranoside. It is proposed to name this compound spongothymidine to indicate its origin and its relationship to thymidine.

(2) Stimson and Reuter, THIS JOURNAL, 67, 847 (1945).

(3) Lythgoe and Todd, J. Chem. Soc., 592 (1944).

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METHYL ETHYL KETONE PHOTOCHEMICAL PROCESSES

Sir:

In view of the recent publication by Durham, Martin and Sutton,[1] of preliminary results on the ratio of ethyl radical to methyl radical formation in the photolysis of methyl ethyl ketone, it may be well to report certain of the results of our study[2] of the photolysis of this ketone at 3130 and 2654 Å.

(1) R. W. Durham, G. R. Martin and H. C. Sutton, Nature, 164, 1052 (1949).

(2) J. N. Pitts, doctoral dissertation, University of California, Los Angeles, July, 1949.
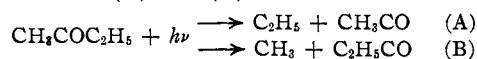
Methyl ethyl ketone–iodine mixtures were irradiated in the vapor phase in a manner similar to that described by Gorin[3] and later extend by Blacet and co-workers.[4,5] Alkyl radicals formed in the primary reactions were "trapped" by iodine and the quantum yields of methyl and ethyl iodide formed in this fashion were obtained with the aid of a mass spectrometer. As a check, quantum yields of the total alkyl iodides were determined by a micro chemical procedure involving titration of the iodides. Analyses of the traces of products pumped off the condensed phase at −75° were carried out with the mass spectrometer and a micro gas analysis apparatus. Some of the significant results obtained are summarized in Table I.

TABLE I

QUANTUM YIELDS OF ORGANIC IODIDES FROM THE PHOTOLYSIS OF METHYL ETHYL KETONE–IODINE MIXTURES AT 3130 AND 2654 Å.

Wave length, Å.	2654	3130	3130
Temp., °C.	100	100	175
Φ CH₃I	0.08	0.01	0.02
Φ C₂H₅I	.44	.40	.43
Φ Total iodides	1.02	.68	.71

If one assumes that the quantum yields of methyl iodide and ethyl iodide are a valid measure of the reactions (A) and (B)

$$CH_3COC_2H_5 + h\nu \begin{array}{l} \longrightarrow C_2H_5 + CH_3CO \quad (A) \\ \longrightarrow CH_3 + C_2H_5CO \quad (B) \end{array}$$

it is evident that at 3130 Å. and 100° process (A) is about forty times as probable as (B), but at 100° and 2654 Å. it is roughly six times as probable.

It was found that the quantum yield of carbon monoxide at 175° and 3130 Å. was only 0.11 compared to that of 0.43 for ethyl iodide. This fact seems good evidence that at this wave length the acetyl radicals are sufficiently stable, even at 175°, so that most of them do not spontaneously decompose on formation, but survive many collisions and react in some other manner. An intensive search utilizing chemical and mass spectrometric methods was made in an effort to detect acetyl iodide which might be expected to be a reaction product, however, no analytical evidence for this compound was found.

In addition to methyl and ethyl iodide, another iodide was found in relatively large amounts. Preliminary chemical and mass spectrometric evidence is indicative of the isopropyl iodide structure, but the results are not as yet conclusive. The quantum yield for "Total iodide" in Table I is the sum of the yields of the latter iodide and those of methyl and ethyl iodides. The quantum yield of the third iodide is apparently temper-

(3) E. Gorin, Acta Physicochimica U. R. S. S., 8, 513 (1938); J. Chem. Phys., 7, 256 (1939).

(4) F. E. Blacet and J. D. Heldman, THIS JOURNAL, 64, 889 (1942).

(5) F. E. Blacet and D. E. Loeffler, ibid., 64, 893 (1942).

ature independent at 3130 Å. If this compound should prove to be isopropyl iodide, a new primary process is indicated in which isopropyl radicals are formed. Further experiments are in progress to establish unequivocally the structure of this iodide and the nature of the reaction by which it is formed.

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THE ISOLATION OF AN ISOMERIC CYTIDYLIC ACID FROM HYDROLYSATES OF YEAST RIBONUCLEIC ACID[1]

Sir:

In search of an explanation for the variations in optical activity reported for different samples of cytidylic acid, from $[\alpha]_D + 36.7°$ to $[\alpha]_D + 49.1°$,[2] we have examined various cytidylic acid fractions isolated from yeast ribonucleic acid hydrolysates. After N acid hydrolysis for one hour and removal of purines with silver sulfate in acid solution, the cytidylic acid fraction was separated from uridylic acid as the insoluble phospho-12-tungstate.[3] Upon recrystallization, the most insoluble fraction was converted to free cytidylic acid which, recrystallized from water, gave a product melting with decomposition at 238–239° (in bath at 230°) and giving $[\alpha]^{23}D + 20.7°$, c, 1.0 in water. *Anal.* Found: N, 12.9; P, 9.75. Calcd. for $C_9H_{14}O_8N_3P$: N, 13.0; P, 9.6. The cytidylic acid obtained from the remaining phosphotungstates gave crystalline fractions ranging in rotation from $[\alpha]_D + 30°$ to $[\alpha]_D + 40°$, consisting evidently of nearly equimolar mixtures of the two isomers, $[\alpha]_D + 20.7°$ and $[\alpha]_D + 49°$. The latter has been obtained from a mixture of dibrucine cytidylate and uridylate by extraction with pyridine and recrystallization of the pyridine insoluble residue from 35% alcohol. A sample with $[\alpha]^{20}D + 49.4°$ decomposed at 233–234° (in bath at 230°). *Anal.* Found: N, 13.06; P, 9.36.

Another sample of yeast ribonucleic acid was hydrolyzed in N sodium hydroxide at room temperature for nineteen hours. The solution was neutralized with formic acid and the nucleotides partly removed on a Dowex-1 formate ion exchange column.[4] The cytidylic acid fraction was eluted with 0.1 N formic acid and again

placed on a Dowex-1 formate column. Elution with 0.05 N formic acid gave effluents with optical density ratios, 278 mμ/260 mμ, in 0.1 N hydrochloric acid ranging from 1.83 to 2.0. Concentration of the fractions giving ratios from 1.83 to 1.89 to dryness and recrystallization of the residue gave a product with $[\alpha]_D + 20.6°$, c, 0.5%. *Anal.* Found: C, 33.26, 33.4; H, 4.34, 4.43; N, 12.97, 13.18. Calcd. for $C_9H_{14}O_8N_3P$: C, 33.4; H, 4.03; N, 13.0. Fractions with ratios from 1.96 to 2.0 treated similarly gave a product with $[\alpha]_D + 49°$, c, 0.5%. The two isomers obtained by these procedures gave similar decomposition points as found above.

The natural cytidylic acid isomer, $[\alpha]_D + 20.6°$, agrees in properties with synthetic cytidine-2-phosphate as given by Gulland, *et al.*[5] Data on the properties of the latter compound, however, are conflicting.[6] The low-rotating compound in our experiments was not oxidized by periodate and, therefore, contained no cytidine-5-phosphate.

The cytidylic acid, $[\alpha]_D + 49°$, on deamination[7] gave a product which could be isolated readily in 87% yield as a dibrucine salt with $[\alpha]_D - 58.7°$, c, 1.0 in pyridine. The solubility of this compound and its rotation are similar to those of the dibrucine salts of both the uridylic acid usually isolated and synthetic uridine-3-phosphate.[6] The low-rotating cytidylic acid on deamination under similar conditions gave a much more soluble brucine salt which has not yet been fully characterized.

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RECEIVED[8] MAY 22, 1950

(5) J. M. Gulland and H. Smith, *J. Chem. Soc.*, 1527 (1948).

(6) A. M. Michelson and A. R. Todd. *ibid.*, 2476 (1949); D. M. Brown, L. J. Haynes and A. R. Todd, *ibid.*, 408 (1950).

(7) H. Bredereck, *Z. physiol. Chem.*, 224, 84 (1934).

(8) The report of the isolation of an isomeric cytidylic acid presented in this paper was first received on February 21, 1950.

HETEROGENEITY IN PYRIMIDINE NUCLEOTIDES

Sir:

Previous communications from this laboratory[1,2,3,4] have presented evidence for isomerism in the naturally occurring purine ribonucleotides, adenylic and guanylic acids, the nature of which remains to be established. The first step in the establishment of this heterogeneity—namely, two peaks in the ion-exchange elution diagram—has now been duplicated in the pyrimidine nucleotides, cytidylic and uridylic acids (see Fig. 1), iso-

(1) Aided by a grant from the Rockefeller Foundation.

(2) G. R. Barker, J. M. Gulland, H. Smith and J. F. Thomas, *J. Chem. Soc.*, 904 (1949); H. Bredereck and G. Richter, *Ber.*, 71, 718 (1938).

(3) H. S. Loring, P. M. Roll and J. G. Pierce, *J. Biol. Chem.*, 174, 729 (1948).

(4) W. E. Cohn, THIS JOURNAL, 71, 2275 (1949).

(1) C. E. Carter and W. E. Cohn, *Federation Proc.*, 8, 190 (1949).

(2) W. E. Cohn, THIS JOURNAL, 71, 2275 (1949).

(3) W. E. Cohn, *ibid.*, 72, 1471 (1950).

(4) C. E. Carter, *ibid.*, 72, 1466 (1950).