Table I. Relative Abundances of the $P_3H_x^+$ and $P_2H_x^+$ Ions from P_3H_5

Ion mass	Rel abundance at 70 ev
98	100
97	3
96	4
95	7
94	11
93	54
66	72[a]
65	29[a]
64	61[a]
63	67[a]
62	88[a]

[a] Contribution due to P_2H_4 unknown.

$P_3H_5^+$ was found to be 0.3 ± 0.2 ev less than the appearance potential of $P_2H_4^+$ from diphosphine ($I(P_3H_5)$ = 9.1 ev, $I(P_2H_4)$ = 9.4 ev).[13] One would expect the ionization potential of P_3H_5 to be slightly less than that of P_2H_4, whereas if $P_3H_5^+$ were a fragment ion a higher appearance potential might well be expected. Finally, the intensity of $P_2H_3^+$ is substantial even if one assigns $P_2H_4^+$ completely to P_2H_4.[12] If the triphosphine is P_3H_5, the simple loss of a PH_2 group from $P_3H_5^+$ would yield $P_2H_3^+$. Thus the intensity of $P_2H_3^+$ is also consistent with this interpretation.

On the basis of these experiments it is concluded that triphosphine, P_3H_5, is formed during the pyrolysis of diphosphine. Not only does the formation of this compound point out an additional step in the net pyrolytic reaction to produce PH_3 and the polymer P_2H,[2] but it also should provide a means to obtain further insight into the chemistry of the hydrides of phosphorus.

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(13) The method used is given in S. N. Foner and R. L. Hudson, *J. Chem. Phys.*, **25**, 602 (1956).

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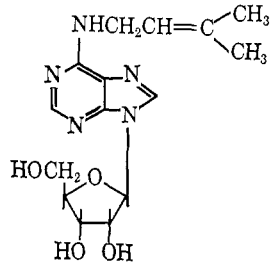
Isolation of N^6-(γ,γ-Dimethylallyl)adenosine from Soluble Ribonucleic Acid[1]

Sir:

We wish to report the isolation of a nucleoside from yeast soluble ribonucleic acid (s-RNA) which has been identified as 6-N-(3-methyl-2-butenylamino)-9-β-D-ribofuranosylpurine (I). Soluble RNA was extracted from Bakers' yeast according to the method of Holley.[2]



I

The s-RNA was hydrolyzed enzymically to its constituent nucleosides and this mixture was resolved by means of partition chromatography on columns.[3] The separated nucleoside was crystallized from acetonitrile–ethanol, 3:1; mp 139°. The crystalline product was homogeneous when chromatographed in solvent systems A–E listed in ref 3. Fifteen milligrams was obtained from 60 g of s-RNA; $[\alpha]^{25}_{546}$ −100° (*c* 0.07, ethanol). *Anal.* Calcd for $C_{15}H_{21}N_5O_4$ (mol wt 335.4): C, 53.72; H, 6.31; N, 20.89. Found: C, 53.68; H, 6.25; N, 20.36. The ultraviolet absorption spectra [$\lambda_{max}^{pH\ 1}$ 265 mμ (ε 20,300), $\lambda_{max}^{pH\ 7-12}$ 269 mμ (ε 19,900)] are indicative of an N^6-(alkyl-substituted) adenosine. The nmr spectrum obtained in deuterated acetone–deuterium oxide solution exhibited the basic pattern associated with adenosine and in addition showed the following peaks: a split peak at δ 1.75 integrating for six protons (two vinyl methyl groups), a multiplet centered at δ 5.4 integrating for one proton (vinyl proton), and a multiplet centered at δ 4.2 integrating for three protons which presumably is due to the methylene group attached to N^6 and the C_4 proton of ribose. The mass spectrum of this compound showed a parent peak at *m/e* 335 and significant peaks at *m/e* 292 and at 203 (free base). There are also prominent peaks at *m/e* 188, 160, 148, 136, and 135 (adenine), and this general fragmentation pattern is identical with that reported for 6-N-(4-hydroxy-3-methyl-2-butenylamino)purine.[4] All of these data are consistent with the assignment of structure I to the isolated natural product.

In order to provide direct confirmation of this structure assignment, we synthesized compound I. β,β-Dimethylacrylonitrile[5] was reduced with lithium aluminum hydride to afford γ,γ-dimethylallylamine, bp 110° (reported 110.5°).[6] The amine was condensed with 6-chloro-9-β-D-ribofuranosylpurine[7] in refluxing ethanol to yield (96%) a product which after three crystallizations from acetonitrile–ethanol (3:1) gave white needles, mp 145–147°; $[\alpha]^{25}_{546}$ −97° (*c* 0.07, ethanol). *Anal.* Found: C, 53.50, H, 6.36, N, 21.01. Ultraviolet spectra showed $\lambda_{max}^{pH\ 1}$ 265 mμ

(1) This research was partially supported by grants from the National Cancer Institute, U. S. Public Health Service (CA-04640 and CA-05697). Melting points are corrected. Nmr spectra were run on a Varian Model HA-100 spectrometer through the courtesy of Mr. Ross Pitcher of Varian Associates. Ultraviolet spectra were obtained on a Cary Model 14 spectrophotometer, infrared spectra on a Beckman Model 9 instrument, mass spectra on a Hitachi Perkin-Elmer RMU-6D instrument (Morgan Schaffer Corp., Montreal), and optical rotations on a Bendix-Ericson polarimeter. Microanalyses were performed by Galbraith Laboratories, Inc.

(2) R. W. Holley, *Biochem. Biophys. Res. Commun.*, **10**, 186 (1963).

(3) The hydrolysis and isolation method has been described previously: R. H. Hall, *Biochemistry*, **4**, 661 (1965). Compound I was found in the fraction corresponding to peak 1, Figure 1, of this reference.

(4) D. S. Letham, J. S. Shannon, and I. R. McDonald, *Proc. Chem. Soc.*, 230 (1964).

(5) K & K Laboratories, Inc.

(6) D. Semenow, C.-H. Shih, and W. G. Young, *J. Am. Chem. Soc.*, **80**, 5472 (1958).

(7) This sample was generously supplied by the Cancer Chemotherapy Service Center of the National Cancer Institute, U. S. Public Health Service.

(ϵ 20,400), $\lambda_{max}^{pH\ 7-12}$ 269 mμ (ϵ 20,000). The infrared spectra of the synthetic compound and that of the isolated compound are superimposable in every detail.

The isolated product was converted to the free base by first treating it with a 3-mole excess of periodate in neutral aqueous solution, then heating the reaction mixture at 100° for 30 min in 0.1 *N* sodium hydroxide solution. The free base cochromatographed in solvent systems A–E (ref 3) with 6-N-(3-methyl-2-butenylamino)purine. This sample was synthesized by condensing the corresponding amine with 6-chloropurine, mp 212–214° (reported 213–215).[8] *Anal.* Calcd for $C_{10}H_{13}N_5$: C, 59.09; H, 6.45; N, 34.46. Found: C, 59.02; H, 6.34; N, 34.65. When compound I is hydrolyzed in 1 *N* hydrochloric acid for 15 min at 100°, the free base of I is not obtained but rather two new bases are formed. These products, termed A and B for the sake of discussion, have been partially characterized.

Compound A was crystallized from ethanol, mp 200–202° dec. *Anal.* Found: C, 58.95; H, 6.58; N, 34.60. Ultraviolet absorption spectra showed $\lambda_{max}^{pH\ 1.5}$ 264 mμ (ϵ 14,750), $\lambda_{max}^{pH\ 7.0}$ 270 mμ (ϵ 13,120), $\lambda_{max}^{pH\ 11.8}$ 276 mμ (ϵ 14,700). The elemental analysis fits the empirical formula of the free base of I, and since the spectra are similar to those of N^1,N^6-dimethyladenine,[9] compound A probably has a cyclized side chain attached to the N^1 and N^6 position of adenine. The formation of such a product would be analogous to the formation of pyrotriacanthine from triacanthine, 6-amino-3-(3-methyl-2-butenyl)purine, under acidic conditions.[10] Compound B was crystallized from acetonitrile–ethanol (1:1), mp 173–174°. *Anal.* Calcd for $C_{10}H_{15}N_5O$ (mol wt 221.26): C, 54.28; H, 6.83; N, 31.66; Found: C, 54.71; H, 6.77; N, 31.24. The ultraviolet absorption spectra [$\lambda_{max}^{pH\ 1.0}$ 272 mμ (ϵ 16,800), $\lambda_{max}^{pH\ 7.0}$ 268 mμ (ϵ 17,700), $\lambda_{max}^{pH\ 11.5}$ 274 mμ (ϵ 17,300)] are similar to those of an N^6-(alkyl-substituted) adenine. The mass spectrum shows a parent peak at *m/e* 221 and major peaks at *m/e* 203 (loss of H_2O) and 162 (loss of $(CH_3)_2COH$). These data suggest that compound B is a product formed by addition of water according to the Markovnikov rule to the double bond of the isopentenyl side chain. Further work on the chemistry of these compounds is in progress and will be communicated shortly.

The amount of compound I in yeast s-RNA was estimated more accurately by spectrophotometric analysis of the initial column isolate. It comprises 0.1 mole % of the nucleotides. We also isolated compound I from s-RNA prepared from calf liver.[11] It is present at a level of 0.05 mole %. Compound I can occur, statistically, in only certain s-RNA molecules and it is of interest that it occurs in serine transfer RNA.[12] Although the isolated natural product has structure I, it is conceivable that in the s-RNA molecule it could exist as the N^1 isomer since N^1-methyladenosine can rearrange to N^6-methyladenosine under alkaline conditions.[13] We cannot rule out the possibility that an analogous rearrangement occurs under the conditions of enzymic hydrolysis of s-RNA.

The occurrence of natural compounds containing an isopentenyl unit attached to adenine has been reported previously. 6-N-(4-Hydroxy-3-methyl-2-butenylamino)purine, called zeatin, occurs in *Zea mays*.[4] 6-Amino-3-(3-methyl-2-butenyl)purine, termed triacanthine, occurs in *Gleditsia triacanthos*.[10] Leonard and Fujii have synthesized the N isomers of triacanthine including the N^6 isomer,[8] the free base of compound I. This synthetic compound is a more potent cytokinin than kinetin [6-furfurylamino)purine].[14]

Compound I, which possesses cytokinin activity,[15] represents the first naturally occurring cytokinin to be found as an integral part of a nucleic acid. Whether there is any relationship between the capacity of compound I to promote cell division and differentiation in plants and its presence in RNA is an open question. Nevertheless, the chemical reactivity of the isoprene–adenine unit may be of considerable importance to the biochemical function of those s-RNA molecules in which it is located.

(8) N. J. Leonard and T. Fujii, *Proc. Natl. Acad. Sci. U. S.*, **51**, 73 (1964).
(9) A. D. Broom, L. B. Townsend, J. W. Jones, and R. K. Robins, *Biochemistry*, **3**, 494 (1964).
(10) N. J. Leonard and J. A. Deyrup, *J. Am. Chem. Soc.*, **84**, 2148 (1962).
(11) R. H. Hall, *Biochemistry*, **3**, 876 (1964).
(12) H. G. Zachau, private communication. The material isolated by Dr. Zachau is identical with our isolated sample of compound I on the basis of ultraviolet spectroscopy, cochromatography, and its breakdown in acid to form compounds A and B. Dr. Zachau has independently obtained evidence that supports the structure of I.
(13) P. Brookes and P. D. Lawley, *J. Chem. Soc.*, 539 (1960).
(14) H. Q. Hamzi and F. Skoog, *Proc. Natl. Acad. Sci.* U.S., **51**, 76 (1964).
(15) Full details of the biological activity will be published elsewhere.

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The Structures of Some Presumed 9,10-Dihydro-9,10-*o*-xylyleneanthracene Derivatives. A Case of 1,5 Participation by Bromine in a Free Radical Bromination

Sir:

The synthesis of a number of derivatives of 9,10-dihydro-9,10-*o*-xylyleneanthracene (I) has been reported and a detailed conformational analysis of these compounds has been made on the basis of spectral properties.[1] In the course of a study of various synthetic approaches to 9,10-benzocyclobutenoanthracene,[2] we encountered reactions of some derivatives of I which could not be reconciled with their previously assigned structures. We now wish to report a revision of the structures of all but one of the above derivatives[3] and the transformation of some of these compounds into a novel new hexacyclic hydrocarbon for which we propose the name triskelene (II).[4] In the course of this work an unusual rearrangement reaction has been found in which a bromine-stabilized radical plays a key role.

(1) K. Sisido, R. Noyori, and H. Nozaki, *J. Am. Chem. Soc.*, **84**, 3562 (1962).
(2) M. P. Cava and R. Pohlke, *J. Org. Chem.*, **28**, 1012 (1963).
(3) For the sake of brevity, several compounds described in ref 1 (a diacetate, a diol, a hydroxy ketone, and an acetoxy ketone) are not specifically discussed in this communication, although they must now be regarded as semitriskelene structures since they were all obtained from either Xb or IXb.
(4) Derived from the word *triskelion:* a symbolic figure consisting of three curved branches or bent legs or arms radiating from a center. Its systematic name is: 5,10-(*o*-benzeno)-4b,5,9b,10-tetrahydro-7H-indeno-[2,1-*a*]indene.