^{35}S-thiamine in rat urine is similar to that in guinea pig urine. This is apparently due to the fact that more than 80% of the radioactivity excreted in rat urine is present as ^{35}S-HT whereas in guinea pig urine only about 20% is ^{35}S-HT. This, in turn, indicates that the hydrolytic cleavage of thiamine occurs much more actively in rat than in guinea pig. It should be noted that only about 4% of the administered ^{35}S-thiamine was excreted as unchanged ^{35}S-thiamine in rat and guinea pig urine within 24 hours when a dose of 200 μg. of ^{35}S-thiamine was orally administered.

This data approximately agree with the report of Fukutomi[12] that 5% of the administered thiamine was excreted in rat urine within 5 days when 500 μg. of thiamine was orally administered for 4 days. To know whether or not bacterial thiaminase takes part in hydrolytic cleavage of thiamine in rat, further experiments are now in progress.

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12) H. Fukutomi: Vitamins, **33**, 151 (1966).

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Covalently Hydrated Oxazirino-tetrahydro-*as*-triazines

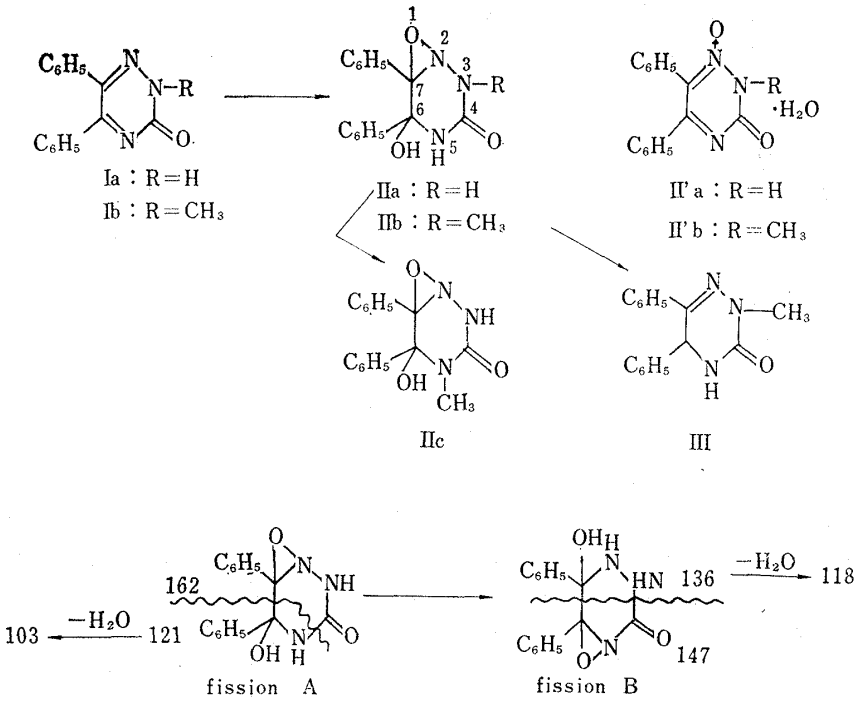
In our previous work,[1] we reported about the oxidation products of 5,6-diphenyl-*as*-triazin-3(2*H*)-one and its 2-methyl analogue with organic peracids, presenting their structures as 5,6-diphenyl-*as*-triazin-3(2*H*)-one 1-oxide mono-hydrate (Ⅱ'a) and its 2-methyl analogue (Ⅱb).

Now, we must revise their structures as 6-hydroxy-6,7-diphenyloxazirino[2,3-*f*]hexahydro-*as*-triazin-4-one (Ⅱa) and its 3-methyl analogue (Ⅱb) on the basis of further chemical and spectroscopical reinvestigations.

The mass spectrum of Ⅱa showed: m/e 283 (M^+), 162, 121 (fission A), 147, 136 (fission B, suggesting a prototropy upon electron impact), 118 and 103, the latter two being understandable as generated by dehydration of the fragment 136 and 121, respectively. The absence of $(M-16)^+$ peak[2] to be formed by deoxygenation of a N-oxide group and of $(M-18)^+$ peak to be generated by dehydration precludes a structure with a N-oxide group and a molecule of water of crystallization for the oxidation products.

Reduction of Ⅱb with lithium aluminum hydride led to 2-methyl-5,6-diphenyl-4,5-dihydro-*as*-triazin-3(2*H*)-one (Ⅲ),[3] indicating the *as*-triazine ring was retained in these oxidation products. Methylation of Ⅱa with methyl iodide in the presence of alkali

1) T. Sasaki and K. Minamoto: This Bulletin, **13**, 1172 (1965).
2) *a*) For identification of the N-oxide group by mass spectrometry, see T.A. Bryce and J.R. Maxwell: Chem. Commun., 206 (1965); *b*) We also observed, without exception, $(M-16)^+$ peak in the mass spectra of *as*-triazine N-oxides we sythesized. The data in this line will be published later.
3) H. Bilz, *et al*: Ann., **339**, 285 (1905).



gave a mono-methylated compound (IIc) [m.p. 193~194°; mixed m.p. with IIb was depressed; NMR ($CDCl_3$): δ 3.37 (3H, singlet, methyl), 7.3~8.3 (10H, phenyl), 10.40 (1H, singlet, NH), 10.81 (1H, singlet, OH)]. The NMR spectrum of IIc is comparable with that of IIb [δ (in dimethyl sulfoxide) 3.11 (3H, singlet, methyl), 7.0~8.2 (10H, phenyl), 10.27 (1H, singlet, NH), 10.68 (1H, singlet, OH)]. The formation of IIc evidenced that IIa and IIb are products covalently hydrated in the position 5 and 6 of the oxazirino-*as*-triazine ring.

The ultraviolet spectra of IIa~c are indicated in Table I with those of the corresponding dihydro-triazinones[4], 5,6-diphenyl-4,5-dihydro-*as*-triazin-3(2*H*)-one (IV), its 2-methyl (III) and 4-methyl analogue (V).

TABLE I. Ultraviolet Absorption Spectra of the Covalently Hydrated Oxazirino-tetrahydro-*as*-triazines and the Corresponding Dihydro-triazinones in Alcohol

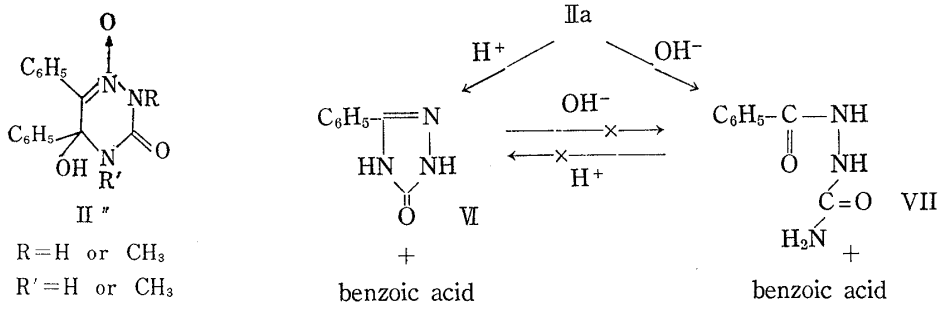
Compounds	mμ (log ε)	References
IIa	236 (4.37), 275*(3.53), 310*(2.91)	1)
IIb	232 (4.41), 272*(3.44)	1)
IIc	231 (4.28), 266*(2.15)	
IV	220*(4.11), 285 (4.06)	
III	220*(4.10), 295 (4.10)	4)
V	220*(4.22), 290 (4.13)	

* refer to inflections

A direct comparison between the absorptions of IIa~c and those of III~V will be rather embarrassing, but an expectation is permissible that if IIa~c were covalently hydrated N-oxides (II'') they would absorb at a significantly longer wave length region than III~V, as indicated by the ultraviolet spectral comparisons between imine N-oxides and isomeric oxaziranes.[5]

4) T. Sasaki and K. Minamoto : To be published in the J. Org. Chem., **31** (12) (1966).
5) W. D. Emmons : J. Am. Chem. Soc., **79**, 5739 (1957).

IIa was hydrolized to 3-hydroxy-5-phenyl-1,2,4-triazole (VI)[6] and benzoic acid in acidic medium, while basic hydrolysis gave 1-benzoyl semicarbazide[7] (VII) and benzoic acid.



It can be stated that VI and VII formed, respectively, *via* independent route, because the conditions where VII was formed could effect no change on VI and on the contrary, VII was not cyclized to VI by the reaction conditions simillar to those where VI resulted from IIa. Analogous degradating reactions were carried out on IIb. Careful considerations on the mechanism of these hydrolysis reactions also suggest the oxazirino-structure of IIa and IIb, on which we will discuss in near future.

It is noteworthy that IIa and IIb are unexpectedly stable and show hardly any chemical properties specific for non-cyclic oxaziranes.[5] Furthermore, the covalent hydrations are extraordinarily rigid; all attempts at dehydration by chemical methods were unsuccessful.

As a conclusion, the "covalently hydrated oxazirino-*as*-triazines" as a whole may be stated as new heterocyclic compounds.

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6) G. Young, *et al.*: J. Chem. Soc., **77**, 224 (1900).
7) O. Widman, *et al.*: Ber., **31**, 378 (1898).

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UDC 547.853.7.07

The Synthesis of 2-Methyl-4-amino-5-β-ethoxyvinylpyrimidine

We have previously reported[1,2] that 2-substituted-4-amino-5-alkoxymethylpyrimidine (I) was readily synthesized by the reaction of amidine and 2-methoxymethylene-3-alkoxy-propionitrile (II).[3] The condensation reactions of II as the three carbon source were also reported.[4]

1) A. Takamizawa, K. Ikawa, K. Tori: Yakugaku Zasshi, **78**, 647 (1958).
2) A. Takamizawa, K. Hirai: This Bulletin, **12**, 393 (1964).
3) A. Takamizawa, K. Hirai, S. Sumimoto: *Ibid.*, **14**, 238 (1966).
4) A. Takamizawa, K. Hirai, Y. Sato, K. Tori: J. Org. Chem., **29**, 1740 (1964).