Experimental[14]

Isolation of I and II——To a solution of 2.4 g of sulfanilamide in 10 ml of 10% HCl, 0.95 g of $NaNO_2$ freshly dissolved in 5 ml of H_2O was added with stirring under ice-water cooling at 5°. To the resulting diazotized sulfanilamide solution, 1 g of 2-OG dissolved in 15 ml of H_2O and 120 ml of the alkaline solution[7] were successively added. The mixture was warmed at 37° for 2 hr, neutralized with 10% HCl with cooling in ice-water and then extracted with 300 ml portions of AcOEt three times. The combined extract was dried over Na_2SO_4 and concentrated below 50° *in vacuo* to almost dryness. The residue was dissolved in 10 ml of MeOH with warming, poured onto a column packed with about 100 g of HCl-treated Al_2O_3[15] and eluted with MeOH to afford two main fractions, from which I and II were separated when the each eluate was concentrated.

I——Orange prisms, mp 266° (from MeOH), yield 50 mg. *Anal.* Calcd. for $C_{14}H_{16}O_4N_6S_2$: C, 42.43; H, 4.07; N, 21.21; MW, 396. Found: C, 42.64; H, 4.17; N, 21.01; MW, 400. UV λ_{max}^{MeOH} nm (ε): 270 (2.1×10^4), 420 (3.2×10^4); λ_{max} (in the alkaline solution[10]) nm (ε): 280 (2.0×10^4), 525 (6.6×10^4).

II——Colorless needles, mp 116° (from benzene), yield 20 mg. *Anal.* Calcd. for $C_6H_6O_2N_4S$: C, 36.37; H, 3.05; N, 28.28. Found: C, 36.43; H, 3.07; N, 27.95. Mass Spectrum *m/e*: 198 (M^+), 170 (M^+-N_2), 157 (M^+-N_3+H, $(C_6H_5SO_2NH_2)^+$), 141 (M^+-N_3-NH, $(C_6H_5SO_2)^+$). UV λ_{max}^{EtOH} nm (ε): 210 (1.6×10^4), 260 (1.7×10^4); λ_{max} (in the alkaline solution[10]) nm: 265, 325.[16]

Isolation of Oxalic Acid——The neutralized reaction mixture remained after the AcOEt extraction of I and II was made slightly alkaline with 10% NH_4OH, to which 10 ml of 10% $CaCl_2$ was added. The precipitate thus separated was filtered, washed with H_2O and dissolved in 30 ml of 10% HCl. The resulting solution was continuously extracted with ether for 5 hr. The extract was dried over Na_2SO_4, concentrated to dryness, and the residue was sublimed above 159° to colorless fine prisms of mp 187° (measured in a sealed capillary tube), whose IR spectrum was entirely identical with that of anhydrous oxalic acid. Yield 30 mg.

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14) UV spectra were measured by a Shimadzu SV-50A Spectrophotometer in a cell of 10 mm optical length, IR spectra by a Nihonbunko 701G IR Spectrometer in KBr pellets, NMR spectra by a JEOL-C60H NMR Spectrometer at 60 MHz with tetramethylsilane as an internal standard and MS by a JEOL 01SG Mass Spectrometer. Molecular weight (MW) was determined by the Rast method using camphorquinone as a solvent. All melting points were uncorrected.

15) Commercial activated Al_2O_3 (Merck, 100 meshes) was dispersed in 20% HCl, allowed to stand for about 50 hr and filtered. After thorough washing with H_2O, it was air-dried and used without activation.

16) II was unstable in the alkaline solution and so the molar absorption coefficient could not be determined precisely.

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Free Radical formed during the Reaction of L-Ascorbic Acid with Hydrazine

Hideo Utsumi, Yutaka Kirino, and Takao Kwan

Faculty of Pharmaceutical Sciences, The University of Tokyo[1]

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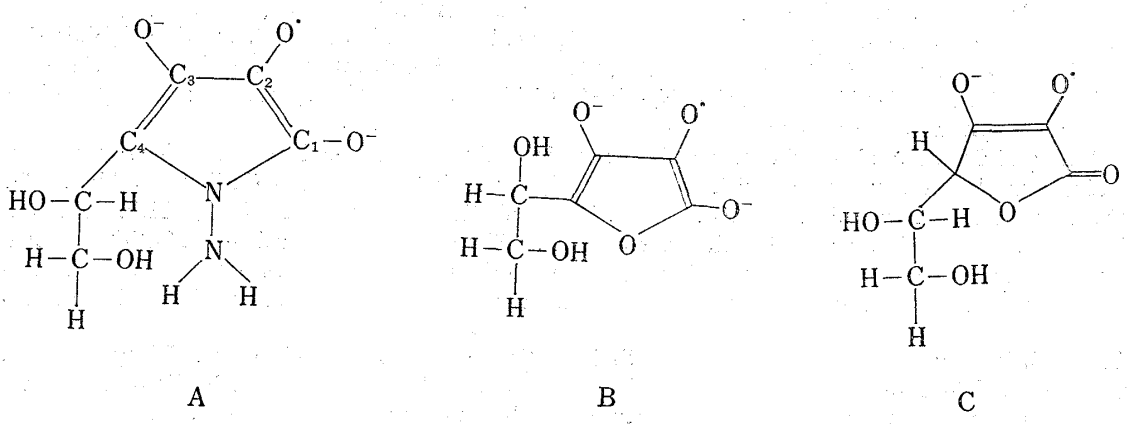
It has been reported by Burlamacchi, *et al.*[2] that an electron spin resonance (ESR) spectrum is observed during the autooxidation of the alkaline aqueous solution of L-ascorbic acid with hydrazine. The spectrum consisted of nine resonance lines probably due to hyperfine

1) Location: *Hongo, Bunkyo-ku, Tokyo.*

2) L. Burlamacchi, P. Sarti-Fantoni, and E. Tiezzi, *Tetrahedron Letters*, **1969**, 5005.

interaction with two non-equivalent nitrogen atoms. If so, it is interesting to note that the ratio of the two nitrogen splittings ($a_{N1}/a_{N2}=2.24$) and the g-value (2.0044) are somewhat different when compared with those of the hydrazyl radical ($a_{N1}/a_{N2}=1.0$—1.5, $g\simeq2.003$[3]) and of the hydrazoxyl radical ($a_{N1}/a_{N2}=10$—20, $g\simeq2.005$[4]).

According to the authors the spectrum was interpreted as due to the structure (A) based on the Russel's structure of mono-dehydro ascorbic acid (B).[5] On the other hand, we have already pointed out that mono-dehydro ascorbic acid is not of the structure (B) but (C).[6] Thus, there remain some doubts about the assignment of the radical species by them. In this report we would like to present some evidences which show that the structure (A) is wrong.



A B C

An alkaline aqueous solution of L-ascorbic acid and hydrazine was prepared by way of adding hydrazine until the solution was adjusted to pH 9. After some dozen hour's exposure to the air at room temperature, ESR spectra were recorded, and found to be identical with that of the Burlamacchi's. A typical spectrum is illustrated in Fig. 1.

Then, dimethyl sulfoxide (DMSO) was employed instead of distilled water as the solvent; the DMSO solution was prepared by adding three times as much hydrazine as L-ascorbic acid by molarity. Leaving it under similar conditions, the spectrum was recorded and found to resemble the one shown in Fig. 1 except for the doublet splitting of each line (Fig. 2).

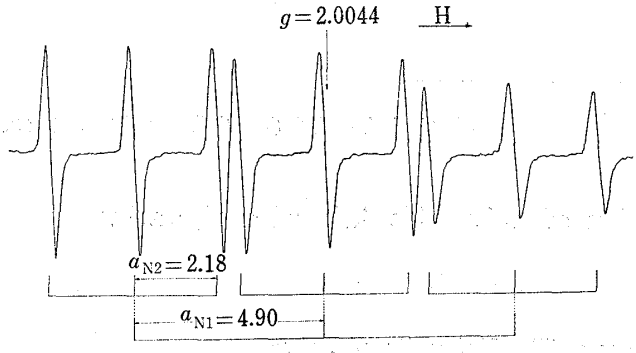


Fig. 1. The ESR Spectrum of Free Radical Formed during the Reaction of L-Ascorbic Acid with Hydrazine in H_2O

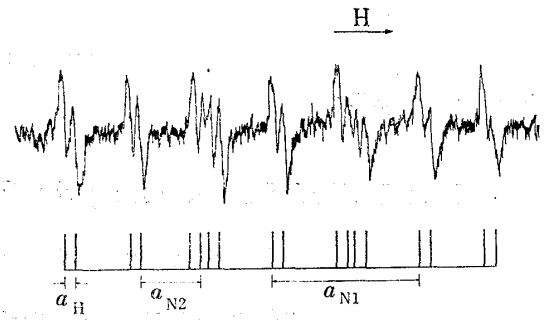


Fig. 2. The ESR Spectrum of Free Radical Formed during the Reaction of L-Ascorbic Acid with Hydrazine in DMSO ($a_{N1}=5.04$G, $a_{N2}=2.22$G, $a_H=0.35$G)

3) V. Malatesta and K.U. Ingold, *Tetrahedron Letters*, **1973**, 3307.
4) S. Terabe and R. Konaka, *J. Am. Chem. Soc.*, **91**, 5655 (1969).
5) G.A. Russel, E.T. Strom, E.R. Talaty, K.-Y. Chang, R.D. Stephens, and M.C. Young, *Record Chem. Progr.* (*Kresge-Hooker Sci. Lib.*), **27**, 3 (1966).
6) Y. Kirino and T. Kwan, *Chem. Pharm. Bull.* (Tokyo), **19**, 718 (1971).

For the purpose of revealing the origin of the doublet splitting, 3-hydroxytetronic acid, which have two hydrogens at the C-4 position, was investigated in place of L-ascorbic acid. As a result, an analogous spectrum was observed with that of Fig. 2, suggesting that the radical species have the same basic structure as that given by the reaction of L-ascorbic acid with hydrazine. The ESR spectrum, shown in Fig. 3, consisted of nine triplets (relative intensities 1:2:1) due to the splitting of the nitrogen hyperfine components by two equivalent hydrogen nuclei. The latter could be ascribed to either the C_4–H_2 of 3-hydroxytetronic acid or the hydrazine N–H_2.

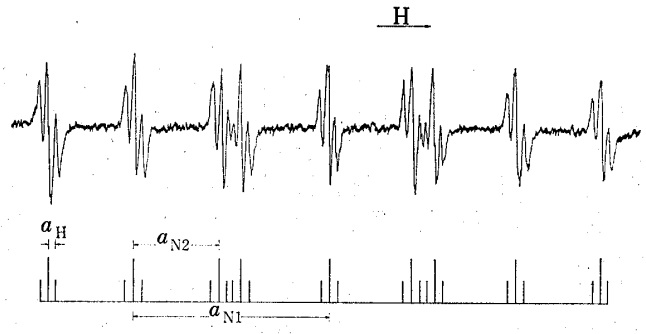


Fig. 3. The ESR Spectrum of 3-Hydroxytetronic Acid–Hydrazine Free Radical in H_2O,D_2O ($a_{N1}=4.85$G, $a_{N2}=2.17$G, $a_H=0.20$G)

When D_2O is used as the solvent, the hydrazine N–H_2 will be substituted by deuterium. The spectrum recorded in D_2O was, however, exactly the same as that given in Fig. 3, proving that the triplet splitting arises from the C_4–H_2 of 3-hydroxytetronic acid. Since the structure (A) has no hydrogen at the C_4 position, it should be excluded. Moreover, during the reaction between triose-reductone and hydrazine, ESR spectra similar to that of Fig. 1 were observed. In this kind of reaction, no pyrrole-ring structure like (A) can be produced.

Further investigations are still continuing as to the possible structure of the radical species produced during the reaction of L-ascorbic acid with hydrazine.

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Addition Reactions of Heterocumulenes. I. Cycloaddition Reaction of Dimethylketene with α-Diimines

Masanori Sakamoto, Kyoko Miyazawa, Yoshiko Ishihara, and Yoshio Tomimatsu

Meiji College of Pharmacy[1]

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The reaction of ketenes with isolated C=N groups to give β-lactam is well known[2] but their reaction with conjugated C=N groups has received little attention. Pfleger and Jäger[3] proposed the structure of the addition reaction product of diphenylketene to N,N′-(dimethylethanediylidene)dianiline (Ia) as the Diels-Alder type, but our examination of the same reaction product found that it is the [2+2] cycloadduct, β-lactam (II).[4]

Recently, Burpitt, *et al.*[5] reported the reaction of dimethylketene with Ia to give 3,4-dihydro-3,3,5,6-tetramethyl-1,4-diphenyl-2(1H)-pyrazinone (IIIa). The structural assignment of IIIa was made on the basis of Pfleger and Jäger's report.[3]

1) Location: *35-23, Nozawa 1-chome, Setagaya-ku, Tokyo.*
2) D.A. Nelson, *Tetrahedron Letters*, **1971**, 2543; A.K. Bose, G. Spiegelman, and M.S. Manhas, *ibid.*, **1971**, 3167.
3) R. Pfleger and A. Jäger, *Chem. Ber.*, **90**, 2460 (1957).
4) M. Sakamoto and Y. Tomimatsu, *Yakugaku Zasshi*, **90**, 1386 (1970).
5) R.D. Burpitt, K.C. Brannock, R.G. Nations, and J.C. Martin, *J. Org. Chem.*, **36**, 2222 (1971).