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The structure of the bicyclic oxidation product of dehydro L-ascorbic acid has been confirmed by detailed mass spectroscopy and  $^{13}\text{C}$  nmr spectroscopy as **3**. This structure was put in doubt, when electron ionization mass spectroscopy detected a molecular peak two mass units higher than expected. Careful experiments at low temperature revealed that the molecular ion disproportionates when heated, giving ion **2** or one of its isomers.

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Upon mild oxidation, sugar osazones undergo cyclization to give the corresponding 2-aryl-4-hydroxyalkyl-1,2,3-triazoles (**2**). On the other hand, dehydro-L-ascorbic acid bisarylhyazones were found to yield, upon mild oxidation, bicyclo compounds of the type **3** (3-6). This cyclization was attributed to the fact that dehydro-L-ascorbic acid bisphenylhydrazone (**1**) exists in equilibrium with a bicyclic hydrazo form (**2**). The hydrazo group of the latter compound, being very susceptible to oxidation to an ozo group, readily loses its two imino protons instead of undergoing cyclization to the triazole (**6**). The oxidized form **3** can also be reduced to the hydrazo form (**2**) which then equilibrates to the monocyclic bishydrazone (**1**) (**6**).

The structure of the bicyclic oxidation product (**3**) was determined by pmr spectroscopy (3,4). Thus, its acetate (**4**) showed one acetyl group and one imino proton, instead of the two acetyl groups and two imino

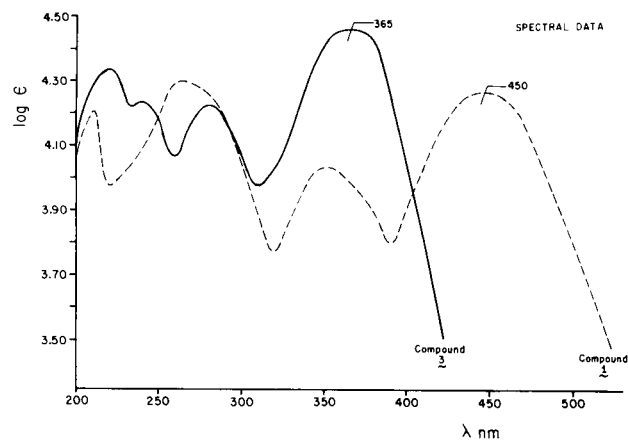


Figure 1. Ultraviolet Spectra of Compounds **1** and **3**.

protons present in the acetate of the parent osazone (**6**).

In a recent study of the mass spectra of dehydro-L-ascorbic acid bisphenylhydrazone (**1**) and its oxidation product (**3**), both mass spectra were surprisingly identical showing a molecular peak at 354, which is the correct mass for compound **1**, and two mass units more than expected for compound **3**. The mass spectrum of acetate **4** showed also a molecular ion two mass units more than calculated (396 instead of 394). High resolution mass spectrometry of compounds **3** confirmed these findings (see Table I). In addition to the molecular peak at 354 corresponding to  $\text{M}^+ + 2$ , a base peak was observed at 247 corresponding to  $\text{C}_{12}\text{H}_{11}\text{N}_2\text{O}_4$ ; this and the other fragments shown in Table I can be accounted for by both

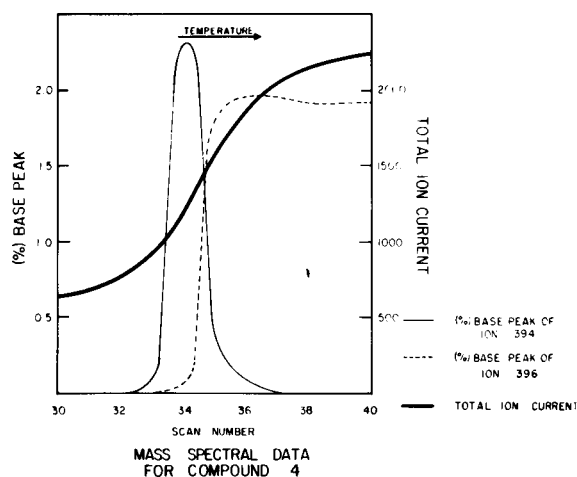


Figure 2. Effect of Temperature on the Mass of the Molecular Ion of Compound **4**.

Table I

High Resolution Mass Spectrum of Compound **3**

Measured Mass	Calculated Mass	Relative Intensity	Formula
354.1298	354.1328	0.36	C <sub>18</sub> H <sub>18</sub> N <sub>4</sub> O <sub>4</sub>
324.1130	524.1110	1.09	C <sub>18</sub> H <sub>16</sub> N <sub>2</sub> O <sub>4</sub>
249.0769	249.0786	1.70	C <sub>10</sub> <sup>13</sup> C <sub>2</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub>
248.0745	248.0746	14.05	C <sub>11</sub> <sup>13</sup> CH <sub>11</sub> N <sub>2</sub> O <sub>4</sub>
247.0713	247.0719	100.00	C <sub>12</sub> H <sub>11</sub> N <sub>2</sub> O <sub>4</sub>
201.0667	201.0664	7.23	C <sub>11</sub> H <sub>9</sub> N <sub>2</sub> O <sub>2</sub>
188.0537	188.0501	1.05	C <sub>9</sub> <sup>13</sup> CH <sub>7</sub> N <sub>2</sub> O <sub>2</sub>
187.0503	187.0508	8.35	C <sub>10</sub> H <sub>7</sub> N <sub>2</sub> O <sub>2</sub>
132.0450		1.06	
119.0605	119.0609	1.58	C <sub>7</sub> H <sub>7</sub> N <sub>2</sub>
105.0442	105.0543	10.22	C <sub>6</sub> H <sub>5</sub> N <sub>2</sub>
94.0623	94.0612	1.43	C <sub>5</sub> <sup>13</sup> CH <sub>7</sub> N
93.0652	93.0578	16.18	C <sub>6</sub> H <sub>7</sub> N
92.0502	92.0500	61.90	C <sub>6</sub> H <sub>6</sub> N
91.0430	91.0422	5.63	C <sub>6</sub> H <sub>5</sub> N
78.0441	78.0425	6.23	C <sub>5</sub> <sup>13</sup> CH <sub>5</sub>
77.0386	77.0391	61.30	C <sub>6</sub> H <sub>5</sub>
76.0307	76.0313	1.06	C <sub>6</sub> H <sub>4</sub>
66.0482	66.0469	1.04	C <sub>5</sub> H <sub>6</sub>
66.0428		1.71	
65.0401	65.0391	29.96	C <sub>5</sub> H <sub>5</sub>
64.0322	64.0313	3.95	C <sub>5</sub> H <sub>4</sub>
63.0239	63.0235	2.71	C <sub>5</sub> H <sub>3</sub>

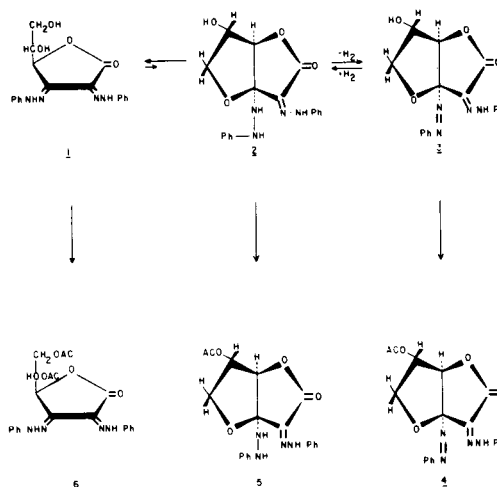
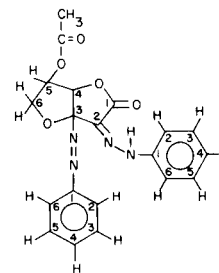


Table II

<sup>13</sup>C Chemical Shifts of Compound **4**  
in PPM Downfield from TMS (a)

Tetronic Ring			2-Phenylhydrazo		
Carbon #	$\delta$		Carbon	$\delta$	
C-1	162.0	(165.4) (b)	C'-1	141.5	(141.9)
C-2	122.5	(123.2)	C'-2,6	114.5	(114.2)
C-3	105.0	(140.2)	C'-3,5	128.5	(129.5)
C-4	83.5	( 76.0)	C'-4	124.0	(120.6)
C-5	73.0	( 67.3)			
C-6	67.5	( 61.9)			
3-Phenylazo			Acetate		
C'-1	151.0	(143.6)	CH <sub>3</sub> -	17.0	
			O		
C'-2,6	122.5	(112.6)	-C-	169.0	
C'-3,5	128.5	(129.2)			
C'-4	131.5	(123.4)			

(a) Deuteriochloroform was used as an internal standard and converted to TMS scale by  $\delta_{\text{TMS}} = \text{deuteriochloroform} + 74.0$ . Error =  $\pm 0.5$  ppm. (b) ( ) Denote  $\delta$  for equivalent carbons in compound **6** (reference 8).

structure **3** and **2**. Thus, the base peak at 247 can correspond to the loss of phenylazo group from compound **3** or a phenylhydrazone group from the reduced form **2**.

Furthermore, although the ultraviolet spectrum of compound **3** shows an absorption maximum at  $\lambda$  365 nm considerably lower than that of the parent bis-hydrazone **1** at  $\lambda$  445 nm (see Figure 1) which agrees with structure **3**, yet this low absorption is not incompatible with structure **2**. In both cases the shift to lower wavelength could be attributed to the disappearance of conjugation with the C-3 hydrazone group in compound **1**.

The persisting doubt about the exact structure of the oxidation product of the dehydro-L-ascorbic acid bis-hydrazone led us to carry out a more detailed mass spectroscopic study of acetate **4**. The study revealed that, under the normal experimental conditions used to obtain electron impact mass spectra (high total ion current), the molecular ion observed had a mass of 396, which is in agreement with structure **5**, but is two mass units higher than for structure **4**. However, it was observed that the mass spectra obtained under milder conditions, where the temperature of the sample was kept below the decomposition point of the compound, revealed the expected molecular ion for structure **4** at 394. It was further found that when the sample temperature was slowly raised above that of the melting point, the 396 ion started to appear, affording spectra where the 394 peak was accompanied by the 396 ion. Finally, as the tempera-

ture rose further, the 396 ion was the only one observed (see Figure 2). It was concluded that the 396 ion appears only when thermal decomposition of the sample occurred, causing the azo compound **4** to yield compound **5** or an isomer thereof. A slower change can be detected

at room temperature in the electronic absorption spectrum of compound **3**. It was thus found that the absorption spectrum of compound **3** undergoes, over a period of several weeks, a gradual shift of its longer wavelengths absorptions towards lower wavelength.

To confirm structure **3**, we have carried out a  $^{13}\text{C}$  nmr study of acetate **4**. Table II shows the chemical shift of the carbon atoms of compounds **4** and **6**. The carbon atoms were assigned by comparison with the spectrum of compound **6** and from the uncoupled spectrum where coupling with the protons was observed. Thus C-6 appeared as a triplet, C-5, as a doublet, and C-2, C-3, and C-4 were singlets. Although the upfield shifts of C-4 of the sugar ring is consistent with the loss of double bond at this position as in structures **4** and **5** (but not structure **6**), the large downfield shift of the resonances of the phenyl group carbons are incompatible with the hydrozo group linked to a benzene ring such as structure **5**. This would be expected for an azo group as in structure **4**.

In view of the preceding, we can safely state that the structure **3** corresponds to the bicyclic oxidation product of dehydro ascorbic acid bishydrazone and structure **4** to that of its acetate.

#### EXPERIMENTAL

Dehydro-L-ascorbic bisphenylhydrozone (**1**) and its oxidation product (**3**) as well as acetates **4** and **6** were prepared according to previously described procedures (3-7). Ultraviolet-visible spectra were measured in ethanol solutions on a Cary 14 spectrophotometer.

The early mass spectral data for compounds **1**, **3**, **4**, and **6** were obtained on a varian M60 mass spectrometer at MTU. High resolution mass spectra of these compounds was carried out at the Battelle Columbus Laboratory according to the following procedure.

Electron-impact mass spectra were obtained by using an AEI MS-902 mass spectrometer operated at an effective resolving power of approximately 15,000. The samples were introduced

into the ion source by means of a direct-insertion probe while simultaneously bleeding in the reference compound perfluorotributylamine. The signal output from the mass spectrometer was digitized and recorded on magnetic tape for subsequent computer processing. Relative intensities and mass measurements for compound **3** are given in Table I.

The MS-902 is equipped with an SRIC CIS-2 ion source which can be operated in either the electron-impact or chemical-ionization mode. The spectra were recorded at 70-eV, and the ion source temperature was maintained at 150°.

The temperature effect study was carried out in the Department of Chemistry in the University of Cincinnati using a Hitachi type RMU-7 mass spectrometer equipped with VG Data system 2000 computer. The temperature of the sample was increased gradually during which time entire mass spectra were continually being obtained. Increasing temperature corresponds to high scan numbers. Results are shown in Figure 2.

The carbon-13 FT spectra were obtained using a Bruker HFX-90 spectrometer operating at 22.63 MHz. Deuteriochloroform was used as an internal lock. The  $^{13}\text{C}$  nmr data for compound **4** are given in Table II.

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