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NOVEL CAGE-SHAPED COMPOUNDS FROM REDUCTION OF r-2,3-EPOXY-2,3,4, c-4a,5,8,c-8a-HEXAHYDRO-c-5,8-ISOBUTYLIDENE-1,4-NAPHTHOQUINONES

Akitami ICHIHARA*, Hideo KAIBUCHI*, Makio KOBAYASHI*, Kengo ODA*, Sadao SAKAMURA*, Akio FURUSAKI**, and Takeshi MATSUMOTO**

*Department of Agricultural Chemistry, Faculty of Agriculture,

**Department of Chemistry, Faculty of Science,

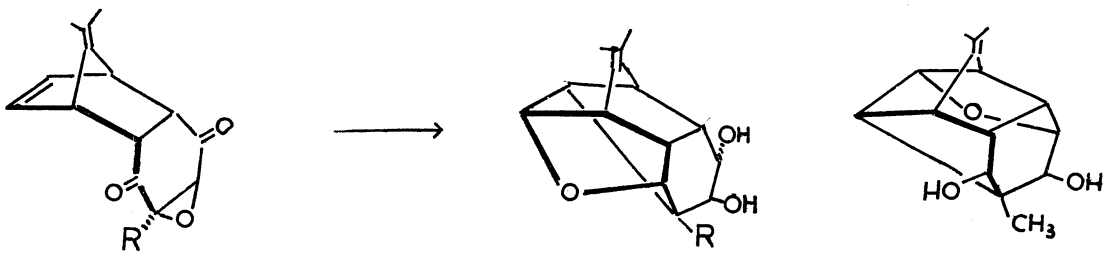
Hokkaido University, Sapporo 060

Novel cage-shaped compounds were obtained by the reduction of r-2,3-epoxy-2,3,4,c-4a,5,8,c-8a-hexahydro-c-5,8-isobutylidene-1,4-naphthoquinones (1) and assigned the structure 2 on the basis of the spectral data and X-ray crystallography. The compounds have an oxygen-containing strained cage structure hitherto unknown.

In the course of the synthetic studies of highly oxygenated cyclohexane derivatives[1], it was found that the reduction of 1a[2] with excess sodium borohydride (8 equivalents) in tetrahydrofuran for 5 hr at room temperature gave an unexpected product 2a, mp 120°C, in 32% yield[3]. The product was analyzed for $C_{15}H_{20}O_3 \cdot \frac{1}{2} H_2O$ and after heating at 90°C, water of crystallization was removed. The spectral data of 2a are as follows : Mass m/e 248 (M^+), IR ν_{max}^{KBr} 3050~3700 (OH), 1075 (tetrahydrofuran), 1055, 1025 (OH), 910 cm^{-1} (tetrahydrofuran), NMR (DMSO) δ 0.78 (3H, s, CH_3), 1.61 (6H, s, $=C(CH_3)_2$), 3.98, 4.23 (1H each, m, CH-O-CH), 4.63 (2H, m, $>$CHOH). Since there are no signals due to vinylic proton in the NMR spectrum, two possible structures, 2a and 3, were deduced.

Acetylation of 2a with acetic anhydride-pyridine gave a diacetate, mp 133°C, $C_{19}H_{24}O_5$, IR ν_{max}^{KBr} 1732, 1233 (OAc), 1075, 912 cm^{-1} (tetrahydrofuran), NMR δ (CCl_4), 0.78 (3H, s, CH_3), 1.68 (6H, s, $=C(CH_3)_2$), 2.20~2.95 (4H, m, $>$CH), 3.97~4.38 (2H, br m, -HC-O-CH-), 4.87 (1H, q, B part of ABX spin system, J_{BA}=5.5 Hz, J_{BX}=1.5 Hz, -CHOAc), 5.13 (1H, d, A part of ABX spin system, J_{AB}=5.5 Hz, CH-OAc).

Since the NMR spectrum of the acetate showed the signals of ABX pattern ascribable to α-protons to acetoxy groups, structure 2a might be plausible for the unex-



1a R=CH_3 2a R=CH_3 3

1b R=CH_2OH 2b R=CH_2OH

pected compound. In fact, the test using periodate gave a positive result which proves the presence of glycol moiety. The same kind of unusual reduction was observed with the analog 1b, yielding product 2b, mp 151°C, $C_{15}H_{20}O_4$, IR ν_{max}^{KBr} 3400, 1050, 1015 cm^{-1}(OH); NMR (DMSO) δ 1.37 (1H, br d, CH), 1.58 (6H, s, $=C<^{CH_3}_{CH_3}$), 1.75~1.97 (1H, m, -CH-), 2.13~2.43 (1H, m, -CH), 2.43~2.80 (2H, m, -CH-), 3.08 (1H, d, J=11 Hz, -CHOH), 3.51 (1H, d, J=11 Hz, CHOH), 3.70 (1H, d, J=6 Hz, >CHOH), 4.02~4.37 (2H, br s, CH-O-CH), triacetate, mp 121°, $C_{21}H_{26}O_7$ ν_{max}^{KBr} 1740 cm^{-1} (OAc), NMR (CCl_4) δ 1.65 (6H, s, $=C<^{CH_3}_{CH_3}$), 1.89, 1.92, 1.96 (3H each, s, $COCH_3$), 2.16~2.95 (4H, m, -CH-), 3.60 (1H, d, J=11 Hz, -CHOH), 4.28 (1H, d, J=11 Hz, -CHOH), 4.20~4.97 (2H, m, -CH-O-CH-), 4.95 (1H, dd, J=6 Hz; J=2 Hz, -CHOAc), 5.27 (1H, d, J=6 Hz, -CHOAc).

The whole structure including stereochemistry of 2a was completely confirmed by the X-ray crystallography. The crystals are monoclinic, with eight molecules of 2a and four molecules of water in a unit cell with the dimensions of a = 32.853 (3), b = 6.003(1), c = 13.713(2) Å, and β=107.80(1)°. The calculated density is 1.281 g/cm^3. The systematic absences, hkl with h+k odd and h0l with l odd, showed the space group to be either Cc or C2/c. At the beginning of the structure determination, the latter was assumed; this choice was confirmed later by successful refinement. Intensities of reflections with 2θ values up to 140° were measured on an automatic four-circle diffractometer using Cu Kα radiation monochromatized with a LiF crystal, and were corrected for the usual Lorentz and polarization factors. Out of the structure factor magnitudes thus obtained, 2280 above 2 (F) were selected for the structural study. The structure was elucidated by

the direct method[4] on the basis of 479 |E| values above 1.30[5]. An E-map calculated with 470 phases contained the whole structure. After the positional and thermal parameters of oxygen and carbon atoms were refined by the least-squares method, a difference Fourier synthesis was carried out. The resulting map yielded the locations of all 21 independent hydrogen atoms. The atomic parameters thus obtained were further refined by the block-diagonal-matrix least-squared method. The R value reached 5.3%. The final coordinates of the non-hydrogen atoms are listed in Table 1. The molecular framework obtained and the bond distances are shown in Figs. 1 and 2, respectively. Thus, the structure of the present molecule has been established as 2a.

Table 1. The final atomic coordinates

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
O(1)	0.13991	0.5270	-0.0498	C(6)	0.13601	0.1860	0.0435
O(2)	0.01535	0.2170	-0.0914	C(7)	0.16465	0.3959	0.0352
O(3)	0.03305	0.1573	0.1444	C(8)	0.16223	0.5290	0.1283
O(W)	0.00000	0.4762	0.2500	C(8a)	0.11210	0.5633	0.0902
C(1)	0.10014	0.5057	-0.0277	C(9)	0.17021	0.3502	0.2089
C(2)	0.09314	0.2505	-0.0381	C(10)	0.20076	0.3290	0.2979
C(3)	0.05381	0.1748	-0.0090	C(11)	0.23449	0.5048	0.3388
C(4)	0.05191	0.2991	0.0858	C(12)	0.20411	0.1294	0.3660
C(4a)	0.09644	0.3746	0.1468	C(13)	0.09184	0.1614	-0.1434
C(5)	0.13261	0.2038	0.1549				

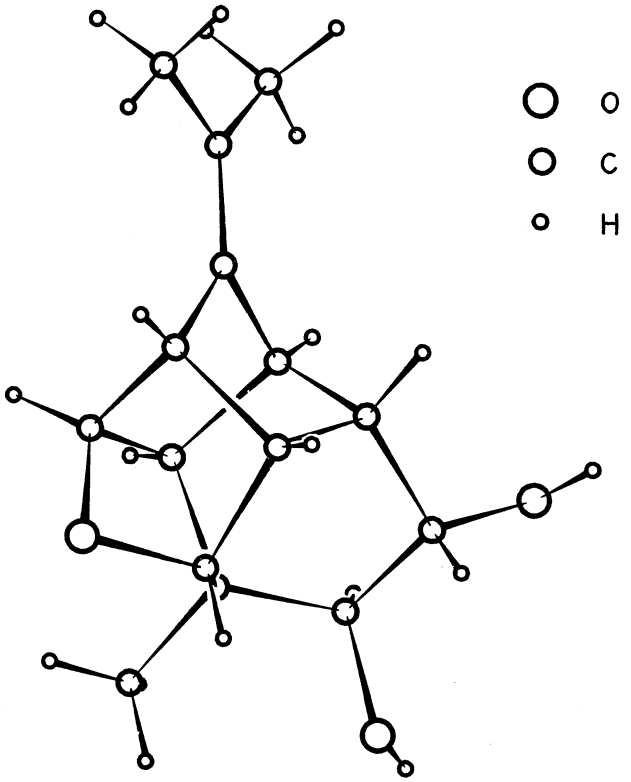


Fig.1. The molecular framework

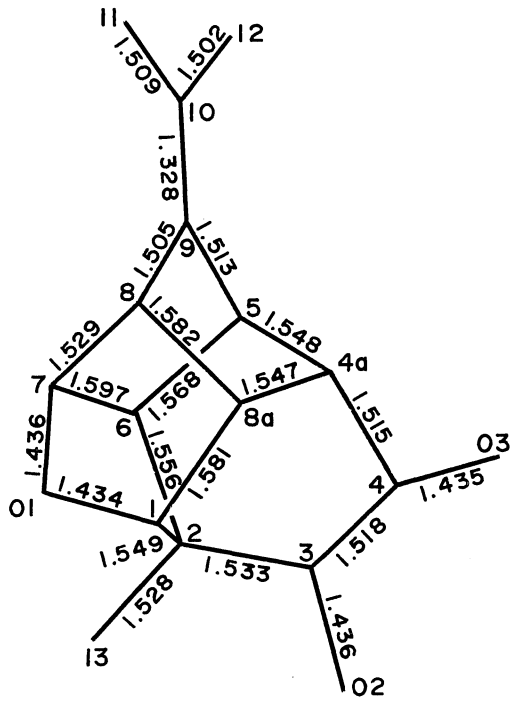


Fig.2. The bond distances (A)

References and Footnotes

1) For a recent publication in this series, see A. Ichihara, K. Oda, M. Kobayashi, and S. Sakamura, Tetrahedron Lett., 4235 (1974) and references cited therein.

2) A. Ichihara, M. Kobayashi, K. Oda, and S. Sakamura, Tetrahedron Lett., 4231 (1974).

3) The same treatment of exo-isomer of 1a gave no corresponding compound.

4) J. Karle and I. L. Karle, Acta Crystallogr., 21, 849 (1966).

5) All calculation were carried out on a FACOM 230-75 computer at the Computing Center of Hokkaido University, using our own programs.

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