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Studies on the Constituents of *Lindera erythrocarpa* Makino. III.[1] The Isolation and Crystal Structure of Sodium Lucidonate

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The crystals of sodium lucidonate dihydrate were isolated from the fruits of *Lindera erythrocarpa* Makino (Lauraceae) and its structure was determined by X-ray analysis. The crystals are orthorhombic with space group $P2_12_12_1$ and unit cell dimensions are $a=15.164(7)$, $b=15.980(7)$, $c=6.242(3)$ Å, $Z=4$. The structure was solved by the direct method and refined by the block-diagonal least-squares method. The final R value for 770 observed structure factors was 0.065. The molecules are linked together by the coordination of oxygen atoms to the sodium ion and by the hydrogen bonds. The coordination number of sodium ion is six.

Keywords——*Lindera erythrocarpa*; sodium lucidonate dihydrate; X-ray analysis; lucidone; coordination of oxygen atoms to sodium ion

The fruits of *Lindera erythrocarpa* Makino (Lauraceae) (Kanakuginoki in Japanese) are used for folk medicine, from which linderone, methyllinderone, lucidone, methyllucidone, kanakugiol, kanakugin and *trans*-cinnamic acid were isolated.[3] Present paper deals with the isolation and structure elucidation of a new compound (I) from the same sauce.

The nuclear magnetic resonance (NMR) spectrum of I resembles that of lucidone (δ 3.76(3H,s,-OMe), 5.18(1H,s,>CH=C<), 7.2—8.4(7H,m,C_6H_5CH=CH–)) and hydrochloric acid treatment of I gives lucidone. The ultraviolet (UV) spectrum of I agrees with that of lucidone in aqueous sodium hydroxide solution (λ_{max} nm 238(ε=27000), 348(ε=25000)). The atomic absorption analysis reveals I to contain about 7% sodium by weight.[4] These data shows that I must be a sodium salt of lucidone.

To establish the structure of I, an X-ray analysis has been undertaken.

Experimental

The fruits of *Lindera erythrocarpa* (500 g) were extracted with ether (600 ml×10). The petroleum ether soluble froction of the extracts was chromatographed on silicic acid (600 g) with petroleum ether, petroleum ether–benzene (1: 1), benzene and benzene–ethylacetate (19: 1). The eluents of benzene–ethylacetate (19: 1) were concentrated and rechromatographed on silicic acid with benzene–ethylacetate (9: 1) and then cellulose powder with chroloform–methanol (10: 1) to afford I (380 mg).

The crystals were grown from methanol as dark yellow prisms. The lattice constants and the intensity data were measured on a Philips four-circle diffractometer using graphite monochromated Cu$K\alpha$ radiation.

Crystal Data——Sodium lucidonate dihydrate, mp 230—240°, $C_{15}H_{11}O_4Na\cdot 2H_2O$, mol. wt=314.27. Orthorhombic, $P2_12_12_1$, $a=15.164(7)$, $b=15.980(7)$, $c=6.242(3)$ Å. $U=1512$ Å^3, $Z=4$, $D_x=1.380$ g cm^{-3}.

A total of 770 independent structure factors were collected within $2\theta=100°$. The intensity data were corrected for Lorentz and polarization factors. A Wilson plot gave an approximate overall temperature factor of 3.3 Å^2.

1) Part II: S-Y. Liu, M. Takai, and Y. Ogihara, *Yakugaku Zasshi*, **96**, 511 (1976).
2) Location: *a) 3-1, Tanabe-dori, Mizuhoku, Nagoya; b) Hongo, Bunkyo-ku, Tokyo.*
3) S-Y. Liu and Y. Ogihara, *Yakugaku Zasshi*, **95**, 114 (1975).
4) Measured by Seiko Atomic Absorption Spectrophotometer, SAS-710.

Determination and Refinement of the Structure——The structure was solved by the multi-solution technique, using the MULTAN program.[5] One of the solutions, based on 161 phases with E values greater than 1.3 gave the E map which showed the locations of 13 non-hydrogen atoms in the molecule. The first Fourier synthesis based upon the coordinates of 13 atoms gave the whole structure.

Refinement of the structure was carried out by the block-diagonal least-squares method using the HLSB program of Okaya and Ashida.[6] 15 Hydrogen atoms could be located on the difference electron density

Table I. Atomic Parameters

(a) Heavy Atoms (Values are $\times 10^4$)

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Na	1850(3)	220(2)	3958(5)	52(2)	39(2)	205(10)	−7(2)	−6(5)	24(4)
C(1)	3759(5)	1029(4)	2662(13)	38(4)	19(4)	165(25)	−10(3)	−3(11)	7(9)
C(2)	4523(6)	1148(5)	1232(14)	43(5)	34(4)	169(26)	−1(4)	−13(11)	23(9)
C(3)	5076(6)	1725(5)	2020(16)	44(5)	29(4)	227(30)	−13(4)	−25(11)	5(8)
C(4)	4655(7)	2063(6)	3987(14)	61(5)	39(4)	140(26)	−13(4)	−56(12)	11(10)
C(5)	3853(5)	1596(5)	4421(13)	42(4)	17(3)	187(27)	−5(3)	4(10)	5(8)
C(6)	3269(5)	1652(5)	6311(13)	40(5)	26(4)	159(23)	−4(3)	−23(11)	−9(9)
C(7)	3390(6)	2338(5)	7696(14)	60(5)	32(4)	159(23)	−1(4)	−7(11)	20(9)
C(8)	2842(7)	2442(5)	9393(15)	65(6)	20(3)	236(30)	4(4)	−41(12)	−11(9)
C(9)	2914(5)	3115(5)	11047(14)	41(5)	26(3)	176(25)	8(3)	−6(10)	13(9)
C(10)	3572(7)	3734(6)	10984(19)	58(6)	34(5)	352(36)	−2(4)	8(13)	−1(11)
C(11)	3599(8)	4366(7)	12617(17)	84(7)	61(6)	268(36)	−12(6)	5(15)	−41(14)
C(12)	2944(7)	4340(6)	14154(20)	67(6)	53(5)	376(37)	4(5)	−44(14)	−30(12)
C(13)	2299(7)	3751(6)	14278(16)	66(6)	59(6)	204(29)	9(5)	−22(12)	−6(10)
C(14)	2295(7)	3119(6)	12643(16)	49(5)	56(5)	247(29)	6(5)	−8(12)	4(12)
C(15)	5318(6)	739(6)	−1869(15)	42(5)	57(5)	154(27)	10(4)	43(11)	15(10)
O(1)	3154(4)	560(3)	2207(8)	50(3)	32(2)	94(15)	−9(2)	20(7)	0(5)
O(2)	4993(5)	2618(4)	4988(10)	71(4)	48(3)	155(17)	−32(3)	−20(8)	1(7)
O(3)	2654(4)	1129(3)	6455(9)	46(3)	37(2)	167(17)	−9(3)	13(7)	−17(5)
O(4)	4557(4)	650(4)	−546(10)	55(3)	35(3)	224(21)	1(3)	3(7)	0(6)
O(5)	865(5)	1115(4)	2170(10)	68(4)	52(4)	225(20)	18(3)	5(8)	20(8)
O(6)	932(5)	1238(4)	7792(10)	70(4)	54(4)	218(21)	16(3)	5(8)	7(8)

Anisotropic Temperature Factors are of the form
$T=\exp-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)$

(b) Hydrogen Atoms (Positional Parameters are $\times 10^3$)

	x	y	z	B(Å^2)
H(1)(C-3)	565(5)	204(5)	183(13)	4.5(1.7)
H(2)(C-7)	390(5)	285(5)	746(14)	5.2(2.0)
H(3)(C-8)	215(5)	198(5)	958(14)	8.7(2.2)
H(4)(C-10)	423(6)	378(6)	1020(16)	6.9(2.5)
H(5)(C-11)	415(7)	469(6)	1285(17)	9.6(2.7)
H(6)(C-12)	281(6)	489(6)	1558(14)	5.4(2.5)
H(7)(C-13)	162(7)	366(6)	1573(16)	9.0(2.9)
H(8)(C-14)	156(6)	271(5)	1286(15)	7.4(2.5)
H(9)(C-15)	609(5)	68(5)	−109(15)	2.3(1.9)
H(10)(C-15)	543(8)	132(6)	−178(21)	16.1(3.5)
H(11)(C-15)	532(8)	35(7)	−233(20)	15.2(3.4)
H(12)(O-5)	89(8)	117(7)	176(18)	14.0(3.3)
H(13)(O-5)	18(7)	130(6)	338(20)	8.8(2.9)
H(14)(O-6)	141(7)	136(6)	758(17)	7.7(3.0)
H(15)(O-6)	53(6)	173(5)	758(17)	9.7(2.5)

5) P. Main, M.M. Woolfson, and G. Germain, "MULTAN, a Computer Program for the Automatic Solution of Crystal Structures," Univs. of York and Leuven, England and Belgium, 1971.
6) Y. Okaya and T. Ashida, "The Universal Crystallographic Computing System," Vol. 1, The Crystallographic Society of Japan, 1967, p. 65.

map calculated at the stage when $R=0.084$. Subsequent least-squares refinement including all the atoms gave the R value of 0.065. The weighting scheme was: $\sqrt{w}=175/Fo$, when $Fo>175$; $\sqrt{w}=1$, when $10<Fo<175$; $\sqrt{w}=0$, when $Fo<10$. The final atomic coordinates are listed in Table I.[7]

Discussion

The present X-ray analysis established the structure of I as sodium lucidonate dihydrate as shown in Fig. 1. Bond lengths and angles are shown in Fig. 1. Standard deviations are estimated to be 2 Å and 0.02°.

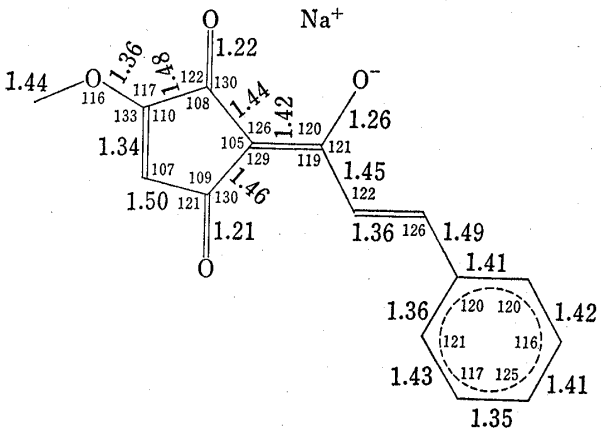


Fig. 1. Bond Lengths (Å) and Angles (°).

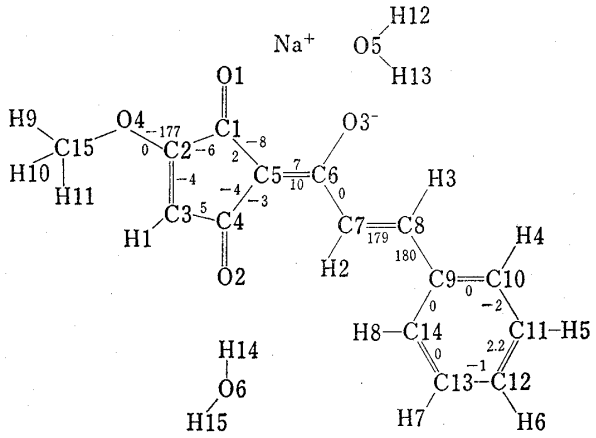


Fig. 2. Torsion Angles (°).

Table II. Least-squares Planes through Various Groups of Atoms and Deviations of Atoms from the Planes

Benzene ring $0.5901x-0.5769y+0.5647z=3.6311$			
C (9)	−0.0011	C (8)	−0.0287
C (10)	−0.0062	C (7)	−0.0401
C (11)	0.0109	C (6)	−0.0398
C (12)	−0.0086	C (5)	−0.0967
C (13)	0.0010	C (4)	0.0376
C (14)	0.0040	C (1)	−0.2775
Cyclopentenedione ring $0.5026x-0.6894y+0.5216z=2.5995$			
C (1)	−0.0014	O (1)	−0.0939
C (2)	−0.0163	O (2)	−0.0543
C (3)	0.0269	O (3)	0.2816
C (4)	−0.0268	O (4)	−0.0208
C (5)	0.0177	C (15)	0.0302
		C (6)	0.0939
		C (7)	−0.0858
		C (8)	−0.0660
Allyl group $0.6098x-0.5719y+0.5487z=3.6273$			
C (5)	−0.0091	C (1)	−0.1797
C (6)	0.0127	C (4)	0.1573
C (7)	0.0067	O (3)	0.0065
C (8)	−0.0144	C (10)	0.0243
C (9)	0.0041	C (14)	−0.0253

Equations of the planes are of the form $AX+BY+CZ=D$, where X, Y, Z and D are in Å units relative to the orthogonal axes $X//a$, $Y//b$, $Z//c$. The least-squares planes are formed by the atoms listed in the left column.

7) Table for the observed and calculated structure factors may be obtained from the first author.

The deviation of atoms from the best planes through the various atoms and the torsion angles are shown in Table II and Fig. 2. The lucidonate ion takes a flat conformation. The methoxyl group also lies on the plane of the cyclopentene dione ring.

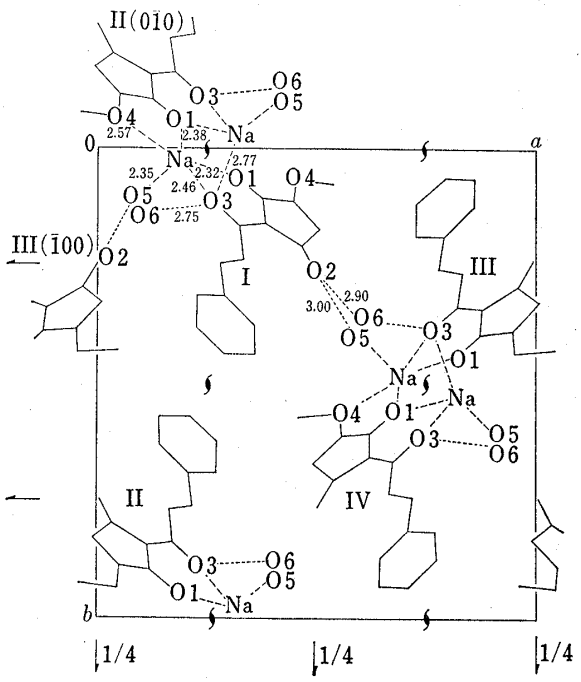


Fig. 3. Projection of the Crystal Structure along the *c* Axis

The position of the molecules are: I at x,y,z; II at $1/2-x, 1-y, 1/2+z$; III at $1/2+x, 1/2-y, 1-z$: IV at $1-x, 1/2+y, 1^1/_2-z$; where x,y and z are the coordinates given in Table I. Hydrogen bonds are shown by dotted lines, and coordinations of oxygen to sodium are shown by broken lines.

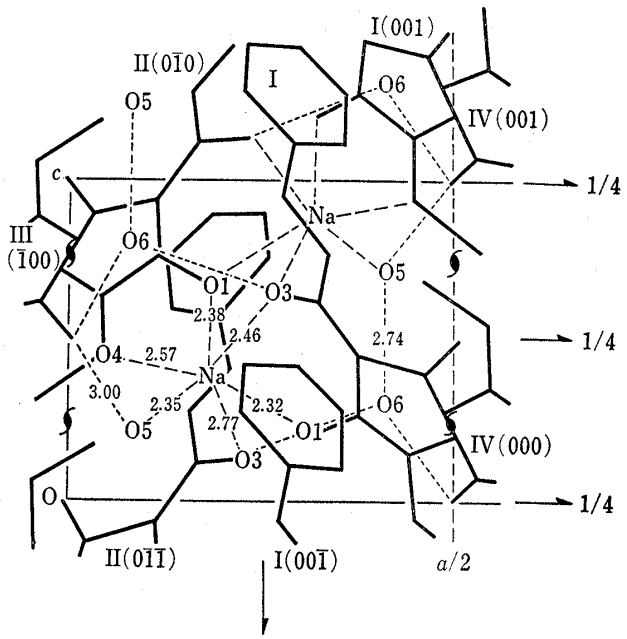
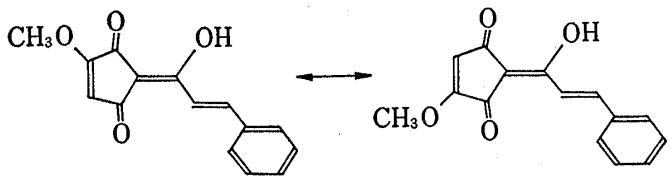


Fig. 4. Projection of the Crystal Structure along the *b* Axis



I Chart 1 II

The projections of the crystal structure viewed along *c* and *b* axes are shown in Fig. 3 and 4 respectively. Five oxigen atoms (O_1,O_1, O_3,O_3,O_4) in the three lucidonate ions and an oxigen atom (O_5) of water coordinate to the sodium ion with the lengths of 2.32—2.77 Å. The coordination number of the sodium ion is six. Another water connects the two lucidonate ions by hydrogen bonds ($O_6\cdots O_3$: 2.75 Å; $O_6\cdots O_2$: 2.90 Å). The molecules are linked together by the coordination and these hydrogen bonds. The lucidone molecule may take two forms I and II and they are in equilibrium in solution (Chart 1).[8] In the crystal of the sodium salt, only the structure of form I was found to exist stabilized by the coordination to the sodium ion.

8) H.H. Lee, *Tetrahedron Letters*, **40**, 4243 (1968).