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Lythraceous Alkaloids. XIII.¹⁾ X-Ray Determination of the Molecular Structures of O-Methyllythranidine N,O,O-Triformate, 22-Bromolythranine N,O,O-Triacetate, and O-Methyldeacetyllythramine

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The crystal and molecular structures of three derivatives of Lythraceous alkaloids, O-methyllythranidine N,O,O-triformate (2), 22-bromolythranine N,O,O-triacetate (3), and O-methyldeacetyl lythramine (4) were determined. The conformational chiralities of the biphenyl group in the crystals of these compounds were in conformity with those proposed on the basis of circular dichroism studies as the predominant forms in solution.

Keywords—Lythraceae; lythranidine; lythranine; lythramine; piperidine alkaloid; X-ray crystallographic analysis; biphenyl; conformational chirality

Lythranine, lythranidine, and lythramine are classified as Lythraceous alkaloids of type A.²⁾ They possess a unique basic skeleton which is regarded as a heteraphane³⁾ having a *meta*-bridged biphenyl moiety and four asymmetric carbon atoms. The biphenyl group is twisted about the bond joining the two rings by repulsion between the substituents at the *ortho* and *ortho'* positions. However, no atropisomerism occurs because of the smallness of the *ortho* substituents of the biphenyl⁴⁾ and the flexibility of the residual part of the macrocyclic ring in these molecules. Thus, rotational isomers differing in the helicity of the biphenyl unit coexist at equilibrium in solution.

From a circular dichroism (CD) spectral study of these alkaloids,¹⁾ the predominant conformational chiralities of the biphenyl groups in solution have been proposed based on the CD spectrum of 22-bromolythranine (1), the absolute configuration of which was elucidated by an X-ray study.⁵⁾ The chiralities assigned for 1, O-methyllythranidine N,O,O-triformate (2), 22-bromolythranine N,O,O-triacetate (3) and O-methyldeacetyllythramine (4) are R, S,

	2	3	4
	$C_{30}H_{37}NO_{7}$	C ₃₄ H ₄₂ BrNO ₈	C ₂₈ H ₃₇ NO ₄ ·CH ₄ O
$F_{\mathbf{W}}$	523.6	672.6	483.6
Crystal system	Monoclinic	Orthorhombic	Monoclinic
Space group	$P2_1$	$P2_{1}2_{1}2_{1}$	$P2_1$
a (Å)	15.569 (2)	17.725 (1)	14.558 (1)
b (Å)	7.439 (1)	17.802 (1)	7.896 (1)
c (Å)	11.876 (1)	10.602 (1)	11.676 (1)
β (*)	94.95 (1)	90.00 (0)	98.04 (1)
\overline{Z}	2	4	2
$D_{\rm x} (\rm gcm^{-3})$	1.269	1.335	1.208
Crystal size (mm)	$0.3 \times 0.2 \times 0.1$	$0.3 \times 0.2 \times 0.1$	$0.3 \times 0.3 \times 0.3$
Number of independ	ent reflections measur	red	
•	2746	3460	2643
Number of reflection	s with non-zero weigh	ht	
used for least-squa	res refinement		
•	2449	3139	2479
R	0.053	0.043	0.035
c^2	0.00251	0.00120	0.00175

TABLE I. Crystallographic Details for 2, 3 and 4

R and S, respectively. Here, we described the crystal structure determination of 2, 3 and 4, undertaken in order to identify the molecular structures representing one of the possible conformations of these molecules.

Experimental

Colorless crystals of 2, 3, and 4 were obtained from methanol solutions. Those of 4 were crystallized in the methanol-solvated form. The unit cell dimensions were determined by least-squares fitting of 2θ values of 20 reflections measured on a Rigaku X-ray diffractometer. Crystal data are listed in Table I.

Three-dimensional intensity data were collected on the diffractometer with graphite-monochromated $CuK\alpha$ radiation ($\lambda = 1.54178$ Å). Integrated intensities were measured in the range of 0.5° with an $\omega = 2\theta$ scan technique, a constant ω scan speed of 0.05° s⁻¹ and an ω scan range of $(1.0+0.2\cdot \tan\theta)$. Backgrounds were counted for 5 s on both sides of each reflection. Three standard reflections monitored every 100 reflections showed no significant change during data collection. All intensities were corrected for Lorentz and polarization factors, but not for absorption effects.

Structure Determination and Refinement

The structures were solved by using the program MULTAN 78.6 The hydrogen atoms were located in each difference electron density map calculated after block-diagonal least-squares refinement of the positional and anisotropic thermal parameters of the non-hydrogen atoms. At the final stage of the refinement including the positional parameters of the hydrogen atoms, the parameter shifts were smaller than half the corresponding standard deviations. The temperature factor of each hydrogen atom was assumed to be equal to the equivalent isotropic, temperature factor of the atom to which it was bound. The function minimized in the refinement was $\sum (w \mid \Delta F \mid^2)$. The weighting scheme was $w = 1/\sigma^2(F_o)$ for observed reflections with $|F_c| \ge \sigma(F_o)$ and $|\Delta F| < 3\sigma(F_o)$, and w = 0 otherwise. $\sigma(F_o)$ was estimated as $\sigma(F_o) = [\sigma_1^2(F_o) + c^2 \mid F_o \mid^2]^{1/2}$, where $\sigma_1(F_o)$ is the standard deviation due to counting errors. The values of R ($= \sum |\Delta F|/\sum |F_o|$) and c^2 at the final stage are given in Table I. The atomic scattering factors were calculated using the analytical expression $f = \sum [a_i \exp(-b_i \lambda^{-2} \sin^2 \theta)] + c \ (i = 1 - 4)$.8

The absolute configuration of 3 was determined by the anomalous-dispersion method, with differences between the intensities of Bijvoet pairs estimated from the counter data measured with Mo $K\alpha$ radiation (λ =0.71069 Å). The values of $\Delta f'$ and $\Delta f''$ used for the bromine atom were -0.374 and 2.456.8 respectively. The computations were done with a FACOM M-150F computer at Shionogi Research Laboratories.9

Results and Discussion

Final atomic coordinates for all atoms except for hydrogens are listed in Table II. The methanol molecule in 4 is represented with C(Me) and O(Me). Perspective views of the respective molecules are given in Figs. 1, 2, and 3. The junction of the oxa-quinolizidine ring

Table II. Fractional Coordinates ($\times 10^4$) of Non-Hydrogen Atoms with Their Estimated Standard Deviations in Parentheses

C(1)	A .	Atom 2			3		4			
C(2) 3443 (3) -2125 (8) 5154 (3) 2512 (2) 5923 (3) 320 (5) 4100 (1) 6908 (4) 5732 (2) C(3) 3481 (3) -3599 (8) 4272 (3) 2557 (2) 6643 (3) 1100 (4) 3272 (1) 6353 (4) 4877 (2) C(4) 4388 (3) -3929 (8) 3933 (3) 2024 (3) 6655 (3) 2242 (5) 3469 (1) 4786 (4) 4184 (2) C(5) 4824 (2) -2312 (8) 3448 (3) 1886 (2) 7464 (2) 2675 (4) 2587 (1) 4152 (4) 3450 (2) C(6) 5668 (3) -2316 (9) 2950 (4) 1352 (3) 7913 (3) 1889 (5) 2740 (2) 2561 (4) 2758 (2) C(7) 5513 (3) -3866 (9) 1855 (4) 1354 (3) 8734 (3) 2255 (6) 2860 (2) 985 (4) 3514 (2) C(8) 4886 (2) -2888 (9) 1018 (3) 1222 (3) 8839 (3) 3662 (6) 2049 (2) 828 (4) 4195 (2) C(10) 3343 (2) -1580 (8) 718 (3) 2539 (2) 8614 (2) 4631 (5) 1065 (1) 2152 (4) 5549 (2) C(10) 3343 (2) -1580 (8) 718 (3) 2539 (2) 8614 (2) 4631 (5) 1065 (1) 2152 (4) 5549 (2) C(11) 2990 (2) -2911 (9) -1844 (3) 2970 (2) 8261 (2) 5705 (5) 1184 (1) 2497 (4) 6857 (2) C(12) 2357 (3) -2098 (10) -1092 (3) 3263 (3) 7463 (3) 5452 (4) 1930 (1) 1389 (4) 7527 (2) C(13) 1404 (2) -1969 (9) -856 (3) 3786 (3) 7151 (3) 6456 (5) 1925 (2) 1381 (4) 8848 (2) C(14) 1189 (2) -700 (0) 64 (3) 4027 (2) 6333 (3) 6211 (4) 1955 (1) 3118 (0) 9390 (1) C(15) 1011 (2) 1079 (8) -134 (3) 4273 (2) 5880 (3) 7182 (4) 1955 (1) 3118 (0) 9390 (1) C(15) 1011 (2) 1079 (8) -134 (3) 4273 (2) 5880 (3) 7182 (4) 1955 (1) 3118 (0) 9390 (1) C(15) 1011 (2) 1079 (8) -134 (3) 4273 (2) 5880 (3) 7182 (4) 1955 (1) 3118 (0) 9390 (1) C(15) 1011 (2) 1079 (8) -134 (3) 4273 (2) 5880 (3) 7182 (4) 1955 (1) 5318 (4) 10537 (2) C(17) 774 (2) 1611 (7) 1819 (3) 4566 (2) 4884 (2) 5728 (4) 1995 (1) 6408 (4) 10337 (2) C(2) (2) 4916 (2) 2010 (3) -2099 (8) 4767 (3) 4750 (2) 4884 (2) 5728 (4) 1995 (1) 6408 (4) 10337 (2) C(2) (2) 116 (2) 116 (8) 1179 (3) 4037 (2) 652 (2) 4995 (4) 4040 (1) 924 (4) 844 (2) (2) (2) 116 (2) 1175 (2) -1425 (8) 5371 (3) 4538 (2) 5114 (2) 2832 (4) 3375 (1) 7118 (4) 10370 (2) (2) 116 (2) 1175 (2) -1425 (8) 5671 (3) 4835 (2) 4918 (2) 2013 (4) 4000 (1) 8370 (2) (2) (2) (2) (2) 116 (3) 4888 (3) 3512 (2) 5144 (2) 2832 (4) 3375 (1) 7118 (4) 9633 (2) (2) (2) (2) (2) (2) (Atom	X		Z	X		Z	X		Z
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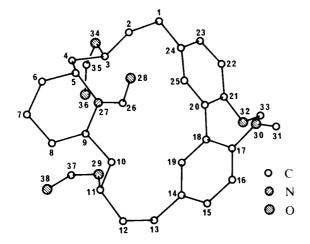


Fig. 1. Perspective View of the Molecule 2

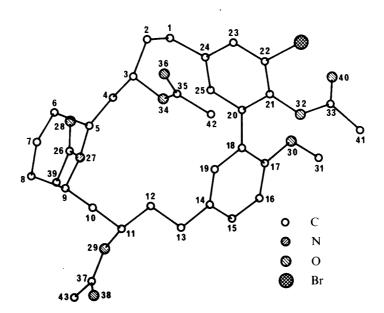


Fig. 2. Perspective View of the Molecule 3

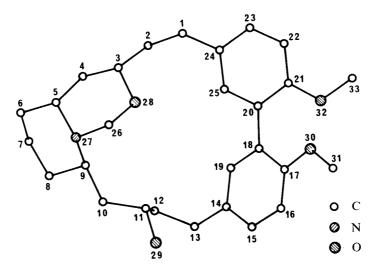


Fig. 3. Perspective View of the Molecule 4

in 4 is cis. The absolute configurations at the chiral centers of 3 are common to those of 1: M helicity for the biphenyl group, and 3S, 5R, 9R, 11S at the asymmetric carbons. For 2 and 4, the chirality of the biphenyl group was determined to be S relative to the asymmetric carbons,

Table III. Molecular Dimensions Relevant to the Biphenyl Groups of 2, 3 and 4

	2	3	4
Dihedral angle between the			
mean planes of the benzene			
rings (~)	81.8 (2)	59.0 (1)	56.1 (1)
Torsion angle (*)			
C(19)-C(18)-C(20)-C(25)	79.9 (7)	-53.9(5)	51.6 (4)
C(16)-C(17)-O(30)-C(31)	-19.7(8)	-12.5(6)	-5.5(5)
C(22)-C(21)-O(32)-C(33)	-3.4(9)	-77.0(5)	6.2 (5)
Interatomic distance (Å)			
C(18)-C(20)	1.495 (7)	1.480 (6)	1.492 (4)
$O(30) \cdot \cdot \cdot O(32)$	3.411 (7)	3.016 (7)	2.868 (4)
Bond angle (1)			
C(16)–C(17)–C(18)	119.4 (5)	119.2 (4)	119.0 (3)
C(16)-C(17)-O(30)	124.8 (5)	124.8 (4)	124.6 (3)
C(18)-C(17)-O(30)	115.8 (5)	116.0 (4)	116.4 (3)
C(17)-C(18)-C(20)	120.0 (5)	125.6 (4)	122.5 (3)
C(19)-C(18)-C(20)	120.9 (5)	115.6 (4)	118.3 (3)
C(17)–C(18)–C(19)	119.0 (5)	118.7 (4)	118.7 (3)
C(18)-C(20)-C(21)	121.3 (5)	124.7 (4)	124.0 (3)
C(18)-C(20)-C(25)	119.4 (5)	117.5 (4)	117.4 (3)
C(21)-C(20)-C(25)	119.3 (5)	117.3 (4)	118.6 (3)
C(20)-C(21)-C(22)	119.0 (5)	119.9 (4)	119.1 (3)
C(20)– $C(21)$ – $O(32)$	115.9 (5)	117.9 (4)	116.7 (3)
C(22)–C(21)–O(32)	125.1 (5)	121.7 (4)	124.2 (3)

TABLE IV. Molecular Dimensions Relevant to the Piperidine Rings of 2, 3 and 4

	2	3	4
Displacement of N(27)			
out of the plane of			
C(5), C(9) and C(26) (Å)	0.144 (5)	0.234 (4)	0.434(3)
Bond distance (Å)			
C(26)–N(27)	1.352 (8)	1.386 (6)	1.457 (4)
Bond angle (')			
C(5)-N(27)-C(9)	114.4 (5)	113.4 (3)	114.3 (3)
C(5)-N(27)-C(26)	119.0 (5)	119.2 (4)	107.2 (3)
C(9)-N(27)-C(26)	123.6 (5)	119.8 (4)	113.7 (3)
Torsion angle (°)			
C(4)-C(5)-N(27)-C(26)	133.6 (6)	-45.5(5)	53.6 (3)
H(C5)-C(5)-N(27)-C(26)	11 (4)	-163(4)	-60(2)
C(10)-C(9)-N(27)-C(26)	-28.1(8)	141.3 (4)	60.8 (4)
H(C9)-C(9)-N(27)-C(26)	-144(3)	28 (3)	-59(2)
N(27)-C(5)-C(6)-C(7)	-53.1(7)	60.7 (5)	-52.3(3)
C(6)-C(5)-N(27)-C(9)	59.5 (6)	-64.5(4)	54.3 (4)
C(5)-C(6)-C(7)-C(8)	52.6 (7)	-55.1(6)	53.4 (3)
C(6)-C(7)-C(8)-C(9)	-54.7(7)	50.0 (7)	-56.0(3)
C(7)-C(8)-C(9)-N(27)	57.6 (6)	-50.0(6)	56.5 (3)
C(8)-C(9)-N(27)-C(5)	-61.3 (6)	58.3 (5)	-55.5 (3)

	2	3	4
Mean e.s.d. value (°)	0.6	0.5	0.3
C(24)-C(1)-C(2)-C(3)	- 55.9	-64.7	116.8
C(1)-C(2)-C(3)-C(4)	-167.3	-54.1	175.4
C(2)-C(3)-C(4)-C(5)	-58.7	-159.4	173.0
C(3)-C(4)-C(5)-N(27)	-47.6	-155.8	-52.3
C(4)-C(5)-N(27)-C(9)	-65.4	165.0	-73.3
C(5)-N(27)-C(9)-C(10)	171.8	-69.4	-175.6
N(27)-C(9)-C(10)-C(11)	-167.0	-70.7	-109.8
C(9)-C(10)-C(11)-C(12)	-175.2	75.1	-58.9
C(10)-C(11)-C(12)-C(13)	-85.2	173.7	-166.6
C(11)-C(12)-C(13)-C(14)	67.0	178.1	-53.0
C(12)-C(13)-C(14)-C(19)	-93.2	25.4	-53.8
C(13)-C(14)-C(19)-C(18)	-179.1	175.9	178.1
C(14)-C(19)-C(18)-C(20)	-177.7	176.6	-171.5
C(19)-C(18)-C(20)-C(25)	79.9	-53.9	51.6
C(18)-C(20)-C(25)-C(24)	-177.8	168.2	-178.3
C(20)-C(25)-C(4)-C(1)	179.6	-176.3	-178.9
C(25)-C(24)-C(1)-C(2)	-22.4	104.0	-60.1

TABLE V. Torsion Angles within the Macrocyclic Rings of 2, 3 and 4

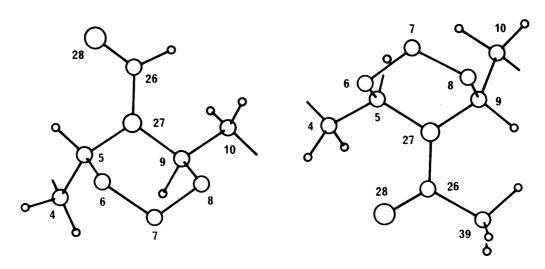


Fig. 4. Structures of the Piperidine Rings of 2 (Left) and 3 (Right)

adopting the same absolute configurations as those of the corresponding atoms in 3. Molecular dimensions relevant to the biphenyl groups and the piperidine rings are presented in Tables III and IV, respectively.

In the crystal of 4, the methanol of solvation joins the two molecules, which are related by a 2_1 axis, by forming the hydrogen bonds of $O(Me) \cdots N(27)$ [2.857 (4) Å] and $O(Me) \cdots O(29)$ (-x, 1/2+y, 1-z) [2.788 (4) Å]. No intermolecular distances shorter than the sums of van der Waals radii are found in 2 and 3.

The benzene rings of the biphenyl group in 2 are markedly twisted about the C(18)–C(20) bond, but those in 3 and 4 are rather less twisted. In the markedly twisted form, the bond angles around C(18) and C(20) deviate little from 120° . However, those in the less twisted form are deformed to reduce the repulsive interaction between O(30) and O(32). Differences among the bond lengths of C(18)–C(20) are not significant. The methyls in methoxyl groups lie approximately on the planes of the benzene rings to which they are bound, but this is not

the case for the acetyl group of 3.

The piperidine rings of all the molecules and the hydrooxazine ring of $\bf 4$ adopt chair forms. The ring conformations in $\bf 2$ and $\bf 3$ are shown in Fig. 4. The N(27) atoms are in nonplanar configurations in spite of the partial double bond character of the amide group,

>N(27):- $\overset{1}{C}$ (26):- $\overset{1}{C}$ (28). This is due to the A^{1.3} type interactions between the group substituted at N(27) and the C(5)- or C(9)-equatorial groups.¹⁰⁾ The bond lengths of N(27)- C(26) are elongated as the planarities of N(27) are decreased on going from 2 to 4 (Table IV). The O(28) atom of 2 and the C(39) methyl group of 3, which are bulky units attached to C(26) in the substituents at N(27), are oriented toward the neighboring equatorial hydrogen atoms [H(5) of 2 and H(9) of 3], not toward the equatorial methylene groups [C(10) of 2 and C(4) of 3]. This seems to play a part in the reduction of A^{1.3} type strain.

Torsion angles within the macrocyclic rings of **2**, **3** and **4** are listed in Table V. Those related to the C(1)—N(27)—C(13) are close to the values for the *gauche* or *trans* conformation, but C(24)–C(1)–C(2)–C(3) [116.8(3)°] and N(27)–C(9)–C(10)–C(11) [109.8(3)°] of **4** are rather close to the value for the partially eclipsed conformation.

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