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An X-Ray Determination of the Structure of Chamaecynenol

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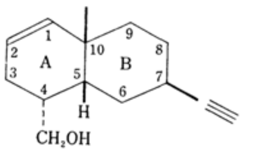
Crystals of chamaecynenol 4-bromo-3-nitrobenzoate, $C_{21}H_{22}O_4NBr$, are monoclinic, with two molecules in a unit cell of the dimensions, $a=10.47$, $b=14.08$, $c=6.75$ Å, and $\beta=101.8°$, and with the space group of $P2_1$. The intensities were recorded on multiple-film equi-inclination Weissenberg photographs and measured visually with a standard scale. The structure was determined by the heavy atom method. The positional and thermal parameters were refined by the least-squares method. The final R factor for the observed reflections is 0.090. The absolute configuration was also determined using anomalous dispersion effect of the bromine atom. It was thus established that chamaecynenol is 7β-ethynyl-4β-hydroxymethyl-10β-methyl-Δ^1-*cis*-octaline in the steroid conformation.

Recently, chamaecynenol $C_{14}H_{20}O$, a novel norsesquiterpenoid, was isolated from the Benihi tree (*Chamaecyparis formosensis* Matsum., Cupressaceae) as a minor constituent.[1] This is an interesting substance as an example of a natural acetylenic compound of terpenoid origin. From chemical and spectroscopic properties, the structure was suspected to be I of the non-steroid *cis*-decalin conformation. However, further chemical investigation was impossible due to too small a quantity of the sample. An X-ray analysis was undertaken in order to reveal such stereochemical details. A heavy atom derivative, chamaecynenol 4-bromo-3-nitrobenzoate, was prepared and supplied by Professor Takase and Dr. Asao.



(I)

Experimental

The compound crystallizes from a benzene solution in the form of colorless plates elongated along the c axis. The unit cell dimensions were determined from zero-layer Weissenberg photographs about the b and the c axes, calibrated with superimposed Al powder photographs.

Equi-inclination Weissenberg photographs were taken at room temperature for the layer lines from 0 to 10 about the b axis and from 0 to 4 about c, using Cu$K\alpha$ radiation. The crystals used had the following maximum and minimum dimensions at right angles to the axis of rotation:

0.01×0.02 cm for the b axis rotation,
0.01×0.03 cm for the c axis rotation.

Intensities were estimated by visual comparison with a standard scale prepared with the same crystals. The multiple-film technique was used to correlate strong and weak reflections, ranging in relative intensities from 8000 to 1. Out of 1982 reflections recorded, about 190 were too weak to be measured. The corrections for the Lorentz and polarization factors were made as usual and those for variation in spot-size in higher layer photographs by the Phillips method.[2] The correction for absorption was neglected.

Crystal Data

The crystallographic and physical data obtained are: Chamaecynenol 4-bromo-3-nitrobenzoate $C_{21}H_{22}O_4NBr$, mp 179—180°C. Monoclinic, $a=10.47$Å, $b=14.08$ Å $c=6.75$ Å, $\beta=101.8°$. Absent spectra, $(0k0)$ when k is odd. Space group, $P2_1$. Two molecules per unit cell. Volume of the unit cell, 974.0 Å^3. Density (by flotation), 1.49_4 g·cm^{-3}. Density (calculated), 1.47_4 g·cm^{-3}. Linear absorption coefficient for Cu$K\alpha$ radiation, $\mu=34.5$ cm^{-1}. Total number of electrons per unit cell, $F(000)=444$.

Structure Determination

The x and z coordinates of the bromine atom were obtained from the Harker section and the y coordinate was set arbitrarily as zero. The four images of the benzene ring were easily picked up by inspecting the sharpened Patterson function around the origin, but it was impossible to select the correct one from the two possible positions of the benzene ring which were related to each other by non-crystallographic two-fold axis in the crystal

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[1] K. Takase, S. Ibe, T. Asao and T. Nozoe, Private Communication.

[2] D. C. Phillips, *ActaC ryst.*, **7**, 746 (1954).

through the bromine atom. The minimum function was formed based on Br–Br vector and it gave the peaks for seven carbon atoms (six ring carbons and a carbonyl carbon) and a nitrogen atom. A three-dimensional Fourier synthesis was made with the phases derived from these nine atoms. An approximate mirror plane was found at $y=0$, due to the predominant contribution from the bromine atom to the phases, and each correct light atom peak in the map was accompanied by a peak of considerable height at the position of mirror image. However, it was possible to assemble a plausible molecular model by selecting them. In order to examine more quantitatively the validity of the model, all possible intra- and intermolecular distances less than 4.0 Å were evaluated. Since no unusual surrounding was found for any of the atoms, the second electron-density distribution was evaluated by taking into account the contribution from all atoms. The resulting map clearly showed the peaks of reasonable height for these atoms, very few background noise peaks being observed.

The positional parameters thus obtained, together with isotropic temperature factors, initially set to 4 Å^2, were refined by block-diagonal matrix least-squares method. After three cycles of refinements,

TABLE 1. FINAL ATOMIC COORDINATES AND TEMPERATURE FACTORS

The anisotropic temperature factors are expressed in the form of $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$.

Atom	x/a	y/b	z/c	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Br	0.1158	0.0000	0.1399	0.01546	0.00456	0.02402	0.00263	−0.00365	0.00423

Atom	x/a	y/b	z/c	B (Å^2)	Atom	x/a	y/b	z/c	B (Å^2)
N	0.1197	0.2255	0.1075	4.26	C(9)	−0.4071	0.0139	−1.3202	3.39
O(1)	−0.1960	0.2078	−0.7406	3.26	C(10)	−0.5027	0.0927	−1.2739	3.01
O(2)	−0.1492	0.3406	−0.5494	3.79	C(11)	−0.2823	0.2685	−0.8920	3.73
O(3)	0.0662	0.2967	0.1661	5.86	C(12)	−0.2752	−0.0784	−0.7848	3.60
O(4)	0.2360	0.2007	0.1772	8.03	C(13)	−0.2461	−0.1349	−0.6531	4.55
C(1)	−0.5175	0.1630	−1.4436	3.83	C(14)	−0.6397	0.0454	−1.2659	5.10
C(2)	−0.4712	0.2503	−1.4307	4.16	C(15)	−0.1412	0.2542	−0.5703	2.94
C(3)	−0.3888	0.2918	−1.2385	4.15	C(16)	−0.0679	0.1908	−0.4100	2.79
C(4)	−0.3364	0.2130	−1.0839	2.81	C(17)	−0.0047	0.2336	−0.2360	2.74
C(5)	−0.4500	0.1386	−1.0672	2.81	C(18)	0.0556	0.1763	−0.0747	2.95
C(6)	−0.4092	0.0672	−0.8981	3.04	C(19)	0.0513	0.0774	−0.0846	3.07
C(7)	−0.3076	−0.0077	−0.9500	3.35	C(20)	−0.0082	0.0350	−0.2665	3.21
C(8)	−0.3675	−0.0604	−1.1503	4.41	C(21)	−0.0662	0.0917	−0.4307	3.31

TABLE 2. ESTIMATED STANDARD DEVIATIONS
($\sigma(x)$, $\sigma(y)$ and $\sigma(z)$ in Å, $\sigma(B)$ in Å^2)

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B_{11})$	$\sigma(B_{22})$	$\sigma(B_{33})$	$\sigma(B_{12})$	$\sigma(B_{13})$	$\sigma(B_{23})$
Br	0.0017	0.0032	0.0014	0.00017	0.00006	0.00029	0.00027	0.00035	0.00037

Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$	Atom	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	$\sigma(B)$
N	0.0125	0.0128	0.0121	0.24	C(9)	0.0118	0.0147	0.0114	0.24
O(1)	0.0087	0.0092	0.0086	0.16	C(10)	0.0123	0.0125	0.0121	0.22
O(2)	0.0095	0.0096	0.0094	0.18	C(11)	0.0139	0.0142	0.0138	0.25
O(3)	0.0121	0.0130	0.0119	0.26	C(12)	0.0137	0.0143	0.0135	0.24
O(4)	0.0152	0.0162	0.0152	0.36	C(13)	0.0161	0.0167	0.0159	0.30
C(1)	0.0144	0.0146	0.0137	0.26	C(14)	0.0169	0.0168	0.0168	0.34
C(2)	0.0151	0.0159	0.0140	0.28	C(15)	0.0126	0.0126	0.0123	0.21
C(3)	0.0150	0.0158	0.0148	0.27	C(16)	0.0121	0.0119	0.0118	0.20
C(4)	0.0120	0.0125	0.0117	0.20	C(17)	0.0119	0.0119	0.0117	0.20
C(5)	0.0119	0.0122	0.0117	0.21	C(18)	0.0125	0.0122	0.0122	0.21
C(6)	0.0127	0.0127	0.0123	0.22	C(19)	0.0126	0.0127	0.0124	0.22
C(7)	0.0113	0.0177	0.0109	0.21	C(20)	0.0129	0.0127	0.0126	0.22
C(8)	0.0159	0.0160	0.0156	0.29	C(21)	0.0130	0.0132	0.0128	0.23

TABLE 3. OBSERVED AND CALCULATED STRUCTURE FACTORS

H	FO	FC
K,L=	0	0
1	46	61
2	39	39
3	18	18
4	35	35
5	36	34
6	10	10
7	0	3
8	16	16
9	3	1
10	3	3
11	0	3
12	0	1
K,L=	0	1
-12	0	4
-11	0	3
-10	9	11
-9	12	14
-8	8	9
-7	11	14
-6	32	27
-5	25	25
-4	12	12
-3	103	104
-2	26	25
-1	41	45
0	62	62
1	3	2
2	48	47
3	39	43
4	35	41
5	13	11
6	0	1
7	25	25
8	12	10
9	7	7
10	4	3
11	0	3
12	5	5
K,L=	0	2
-12	3	2
-11	3	2
-10	4	2
-9	12	12
-8	34	32
-7	21	17
-6	33	26
-5	61	64
-4	21	21
-3	4	10
-2	76	73
-1	49	51
0	28	25
1	56	56
2	48	50
3	42	38
4	0	1
5	10	13
6	27	28
7	24	21
8	0	2
9	15	15
10	18	19
11	10	9
K,L=	0	3
-12	8	9
-11	4	1
-10	0	2
-9	4	5
-8	32	34
-7	9	7
-6	0	1
-5	21	18
-4	35	32
-3	35	33
-2	11	15
-1	26	26
0	61	58
1	50	52
2	20	20
3	7	7
4	26	27
5	28	29
6	18	15
7	4	0
8	0	4
9	4	4
10	2	0
11	2	0
K,L=	0	4
-12	5	5
-11	4	4
-10	7	9
-9	3	1
-8	0	2
-7	0	0
-6	10	9
-5	12	10
-4	11	8
-3	0	1
-2	16	15
-1	36	38
0	34	31
1	12	11
2	13	11
3	23	22
4	46	45
5	38	33
6	24	22
7	8	6
8	9	7
9	9	8
K,L=	0	5
-12	0	1
-11	0	0
-10	0	4
-9	0	3
-8	0	1
-7	3	2
-6	8	7
-5	13	15
-4	4	5
-3	15	15
-2	30	31
-1	28	25
0	19	16
1	28	26
2	28	24
3	17	17
4	12	11
5	9	10
6	10	9
7	10	9
8	2	2
K,L=	0	6
-9	0	3
-8	6	7
-7	7	8
-6	3	1
-5	3	1
-4	16	17
-3	9	12
-2	20	19
-1	5	6
0	16	13
1	12	10
2	4	4
3	6	2
4	3	0
5	6	6
6	13	11
7	4	4
K,L=	0	7
-9	2	3
-8	6	7
-7	0	2
-6	0	6
-5	0	2
-4	11	12
-3	11	13
-2	0	0
-1	7	8
0	12	12
1	7	8
2	8	7
3	10	9
4	6	7
5	12	10
K,L=	0	8
-5	4	6
-4	0	1
-3	3	4
-2	0	4
-1	9	8
0	0	1
1	0	0
2	6	7
K,L=	1	0
1	27	22
2	89	91
3	44	39
4	26	25
5	38	34
6	25	26
7	18	19
8	9	11
9	11	11
10	5	5
11	5	5
12	0	1
K,L=	1	1
-11	0	1
-10	4	2
-9	9	8
-8	14	14
-7	29	28
-6	18	16
-5	31	30
-4	58	49
-3	100	88
-2	157	151
-1	26	20
0	9	14
1	67	66
2	31	27
3	8	6
4	9	8
5	21	22
6	21	20
7	3	2
8	3	3
9	11	11
10	7	7
11	4	3
12	6	7
K,L=	1	2
-11	3	6
-10	11	12
-9	4	5
-8	5	5
-7	13	14
-6	34	33
-5	39	34
-4	40	38
-3	23	21
-2	9	6
-1	36	36
0	76	73
1	32	31
2	17	11
3	40	37
4	41	43
5	22	22
6	5	3
7	14	15
8	19	19
9	9	11
10	8	8
11	6	6
K,L=	1	3
-11	0	2
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-8	18	18
-7	21	23
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-4	19	19
-3	21	20
-2	38	38
-1	34	31
0	12	13
1	28	27
2	38	34
3	26	25
4	20	19
5	0	2
6	22	21
7	27	25
8	24	21
9	5	6
10	0	4
11	5	5
K,L=	1	4
-11	4	7
-10	7	10
-9	0	2
-8	5	5
-7	8	8
-6	14	14
-5	3	4
-4	12	11
-3	16	14
-2	33	35
-1	12	11
0	19	16
1	27	24
2	43	40
3	11	10
4	14	11
5	8	9
6	20	20
7	5	5
8	0	1
9	4	4
10	5	6
K,L=	1	5
-8	9	9
-7	0	5
-6	0	3
-5	15	14
-4	20	21
-3	19	18
-2	8	7
-1	17	15
0	33	32
1	31	27
2	37	32
3	22	18
4	8	7
5	14	13
6	5	5
7	0	2
8	7	6
K,L-	1	6
-6	10	12
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-2	13	12
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6	0	1
7	9	5
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-3	0	4
-2	13	12
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1	10	10
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3	8	8
4	3	4
5	6	5
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-5	4	4
-4	4	5
-3	7	6
-2	0	2
-1	2	0
0	0	3
1	8	8
K,L=	2	0
0	43	54
1	7	6
2	59	57
3	14	9
4	50	47
5	21	20
6	12	12
7	16	17
8	14	15
9	7	8
10	7	8
11	0	3
12	0	1
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-12	2	0
-11	5	6
-10	8	8
-9	0	6
-8	6	7
-7	6	6
-6	23	20
-5	41	42
-4	37	37
-3	42	36
-2	65	61
-1	35	35
0	46	50
1	4	6
2	43	42
3	50	51
4	16	18
5	0	2
6	22	22
7	20	22
8	9	10
9	5	3
10	7	7
11	7	7
12	3	5
K,L=	2	2
-11	5	8
-10	3	3
-9	3	3
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-3	31	31
-2	21	19
-1	24	20
0	21	20
1	8	7
2	58	54
3	38	34
4	14	13
5	25	24
6	16	17
7	9	11
8	0	1
9	5	5
10	7	6
11	5	5
K,L=	2	3
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-6	0	5
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4	22	20
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6	14	16
7	9	10
8	10	10
9	11	13
10	2	1
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K,L=	2	4
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-6	14	16
-5	17	18
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-2	22	21
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2	14	13
3	25	26
4	28	28
5	14	10
6	12	9
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9	2	3
K,L=	2	5
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-1	22	19
0	17	15
1	13	11
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4	11	12
5	10	7
6	8	9
7	8	10
8	7	6
K,L=	2	6
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-3	14	13
-2	16	16
-1	12	9
0	24	22
1	19	19
2	12	12
3	3	2
4	7	5
5	7	8
6	6	7
7	5	4
K,L=	2	7
-9	3	5
-8	7	7
-7	4	3
-6	3	1
-5	3	4
-4	9	8
-3	6	7
-2	0	1
-1	8	7
0	8	9
1	7	8
2	6	6
3	7	5
4	9	8
K,L=	2	8
-5	6	8
-4	2	4
-3	0	2
-2	5	6
-1	6	7
0	4	5
1	2	1
K,L=	3	0
1	42	43
2	66	68
3	37	39
4	19	16
5	13	11
6	15	15
7	17	14
8	16	18
9	7	7
10	5	6
11	0	2
12	5	6
K,L=	3	1
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-11	3	4
-10	5	6
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-5	34	31
-4	42	41
-3	63	62
-2	33	29
-1	33	32
0	44	54
1	58	62
2	49	57
3	15	13
4	36	40
5	58	60
6	28	29
7	9	7
8	0	4
9	10	11
10	4	4
11	0	1
K,L=	3	2
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-11	0	1
-10	0	4
-9	10	10
-8	7	6
-7	13	14
-6	23	23
-5	30	33
-4	31	32
-3	5	7
-2	29	34
-1	41	46
0	61	60
1	29	28
2	19	19
3	9	9
4	28	31
5	18	19
6	6	6
7	7	6
8	8	8
9	9	10
10	4	4
11	3	4
K,L=	3	3
-11	0	3
-10	6	5
-9	3	4
-8	5	4
-7	12	12
-6	12	12
-5	15	15
-4	3	4
-3	23	26
-2	37	38
-1	36	37
0	65	63
1	24	21
2	22	22
3	37	38
4	26	28
5	6	7
6	15	15
7	12	13
8	3	3
9	4	4
10	5	5
K,L=	3	4
-11	4	4
-10	0	2
-9	0	5
-8	10	10
-7	9	11
-6	12	14
-5	0	0
-4	20	21
-3	34	36
-2	20	21
-1	2	0
0	18	18
1	37	34
2	34	32
3	10	11
4	7	8
5	11	10
6	14	16
7	7	8
8	3	3
K,L=	3	5
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-9	0	2
-8	10	10
-7	5	7
-6	3	2
-5	0	2
-4	16	15
-3	6	4
-2	0	0
-1	16	15
0	11	11
1	24	23
2	3	4
3	10	11
4	18	18
5	10	12
6	9	10
7	2	2
8	3	4
K,L=	3	6
-8	6	8
-7	3	4
-6	7	8
-5	8	9
-4	5	4
-3	6	6
-2	12	11
-1	15	15
0	13	12
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K,L=	13	4
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K,L=	14	0
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K,L=	15	0
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4	8	8
K,L=	15	4
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K,L=	16	0
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K,L=	16	2
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1	2	3.

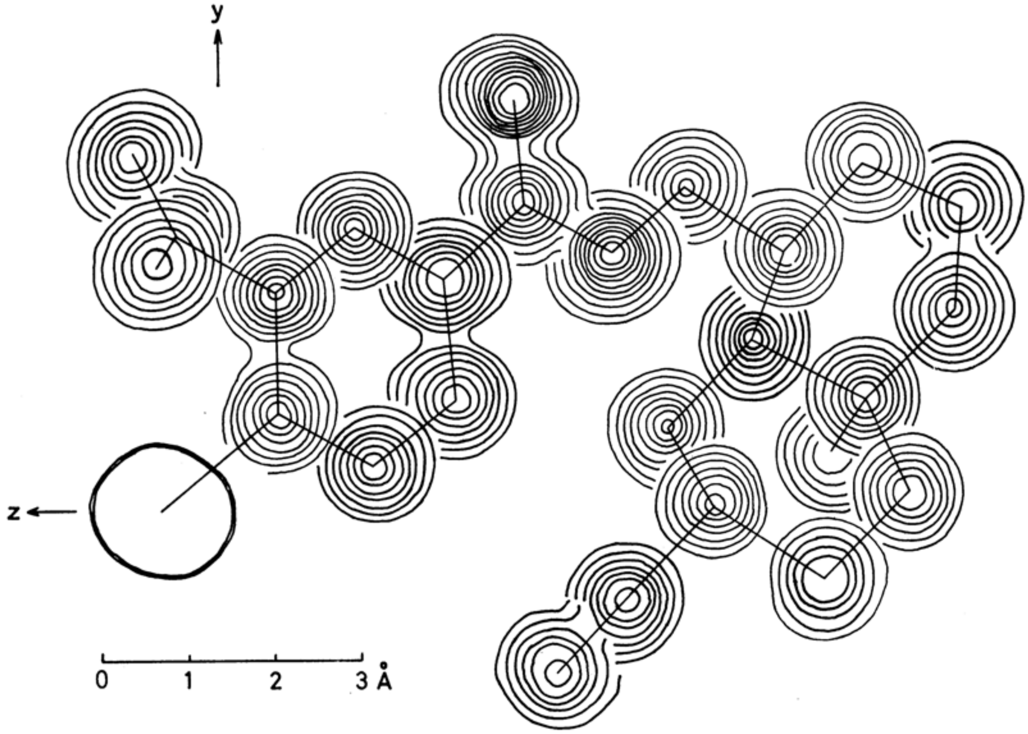

Fig. 1. Composite electron density diagram of sections parallel to (100). The contours are at intervals of 1.0 e. $Å^{-3}$ starting with 1.0 e. $Å^{-3}$. The contours of the bromine atom are omitted.

the discrepancy factor, $R=\sum\|F_o|-|F_c\|/\sum|F_o|$ was about 0.16. At this stage anisotropic temperature factors of the form, $\exp\{-(B_{11}h^2+B_{22}k^2+B_{33}l^2+B_{12}hk+B_{13}hl+B_{23}kl)\}$, were applied for the bromine atom. Four cycles of refinement reduced the R factor to 0.090 for the observed reflections. The atomic scattering factors used in the calculations were taken from the International Tables for X-ray Crystallography (1962).[3] The final atomic coordinates and the temperature factors are given in Table 1, and their standard deviations in Table 2. The observed and calculated structure factors are listed in Table 3. The final three-dimensional electron-density distribution calculated with phases based on these parameters is shown in Fig. 1.

The computations were done on a HITAC 5020 computer in the University of Tokyo with programs written by Dr. T. Ashida.

Determination of Absolute Configuration

After errors caused by neglect of the absorption correction were taken into account, seven sets of Bijvoet pairs were observed to have significantly different intensities in the upper layer photographs around the c axis. For the Bijvoet pairs, $|F(hkl)|$ and $|F(h\bar{k}l)|$ were calculated using $\Delta f'$ and $\Delta f''$

TABLE 4. THE DETERMINATION OF THE ABSOLUTE CONFIGURATION

$h\ k\ l$	Calculated			Observed		
	$\|F(hkl)\|$		$\|F(hkl)\|$	$I(hkl)$		$I(hkl)$
4 1 0	26.2	>	25.2		<	
1 2 0	4.4	<	7.0		>	
4 1 1	8.3	>	6.8		<	
0 1 2	72.8	>	70.7		<	
0 2 2	20.2	<	20.7		>	
1 2 2	5.1	<	9.0		>	
0 2 3	11.3	<	13.8		>	

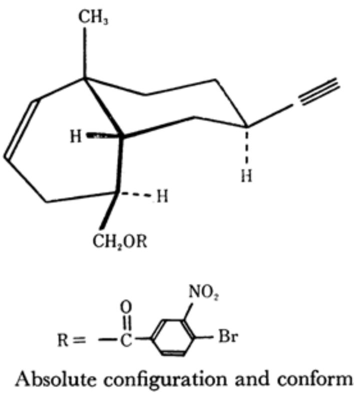

Fig. 2. Absolute configuration and conformation.

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[3] "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England (1962), p. 202.

for the bromine atom on the basis of the model in a right-handed coordinate system. As shown in Table 4, inequality relations in each pair are the reverse of observed and calculated values, so that model used in the calculations is the mirror image of the actual molecule. Therefore, chamaecynenol has the absolute configuration indicated in Fig. 2. The hydroxymethyl group on C(4) and the ethynyl group on C(7) are in the β orientation.

Results and Discussion

Molecular Structure. From the X-ray analysis described in the preceding paragraphs, the steric structure of the molecule has been determined without any ambiguity. The intramolecular bond lengths and angles are shown in Figs. 3 and 4, respectively. The mean estimated standard deviation in a bond length is about 0.020 Å and in a

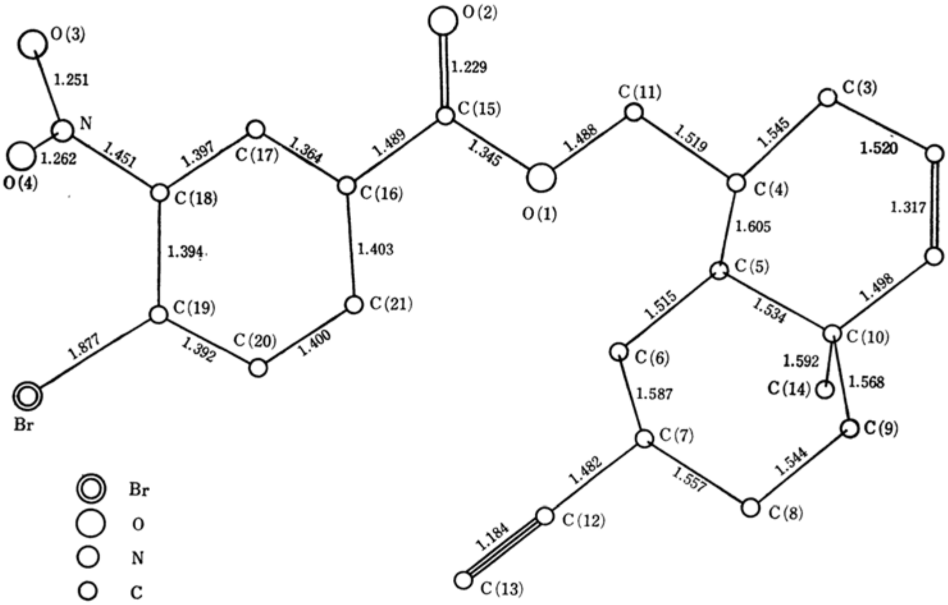


Fig. 3. Bond lengths (Å).

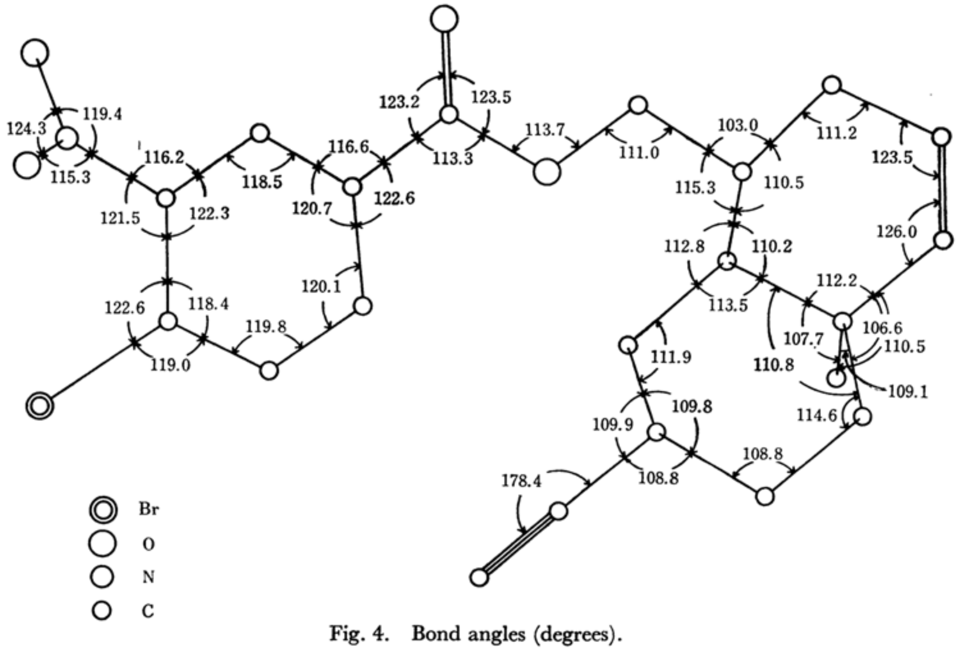
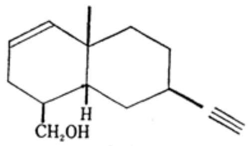


Fig. 4. Bond angles (degrees).



(II)

bond angle about 1.1°. All bond lengths and angles are reasonable within the errors. The locations of the double and the triple bonds are assigned unambiguously, and are the same as those in chamaecynone and isochamaecynone.[4] Thus the chemical structural formula of chamaecynenol has been established as II.

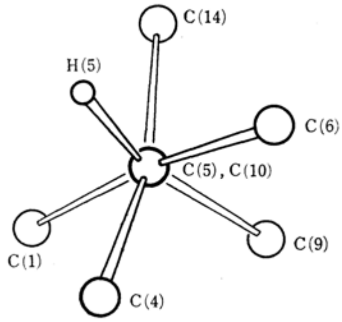


Fig. 5. Conformations about the bond C(5)–C(10).

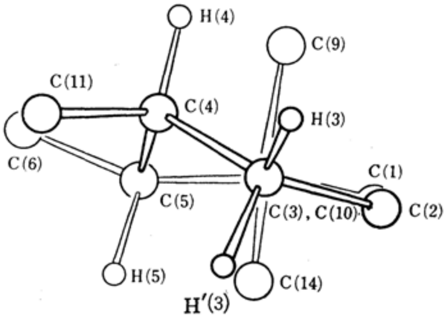


Fig. 6. Ring A, viewed along the line C(3)···C(10).

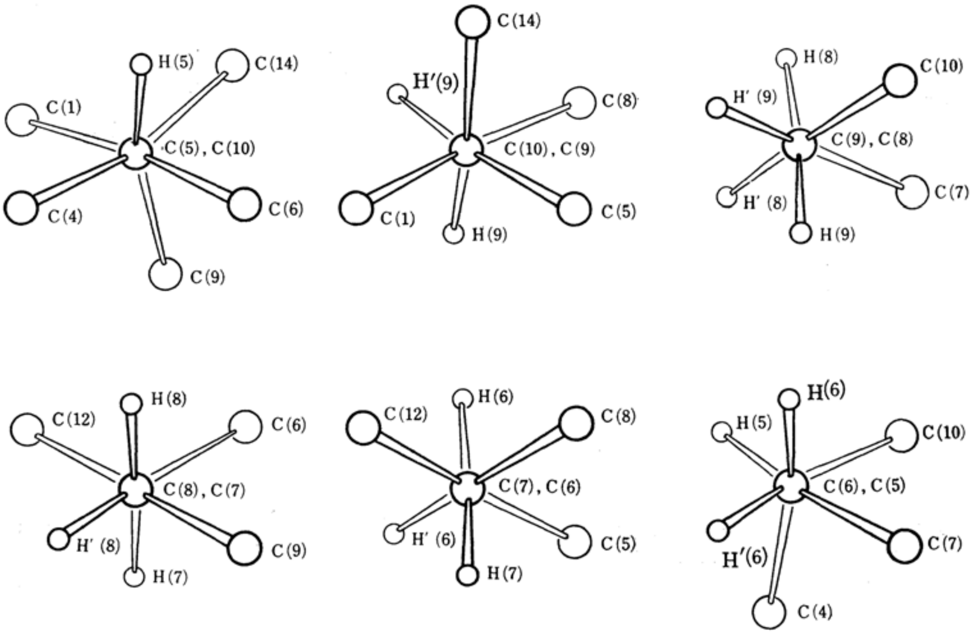


Fig. 7. Conformations about the six single bonds of ring B.

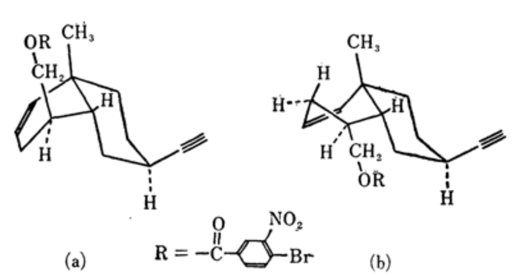


Fig. 8.

Conformation. A view along C(5)–C(10) in Fig. 5[5] shows that the ring system is cis fused and in the steroid conformation. The ring A is half-chair as shown in Fig. 6. The conformations about the six single bonds in the ring B are shown in Fig. 7; all are seen to be staggered, and the

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[4] T. Nozoe, Y. S. Cheng and T. Toda, *Tetrahedron Letters*, **1966**, 3663.

[5] In the preparation of this and other figures, the positions of the hydrogen atoms were assumed.

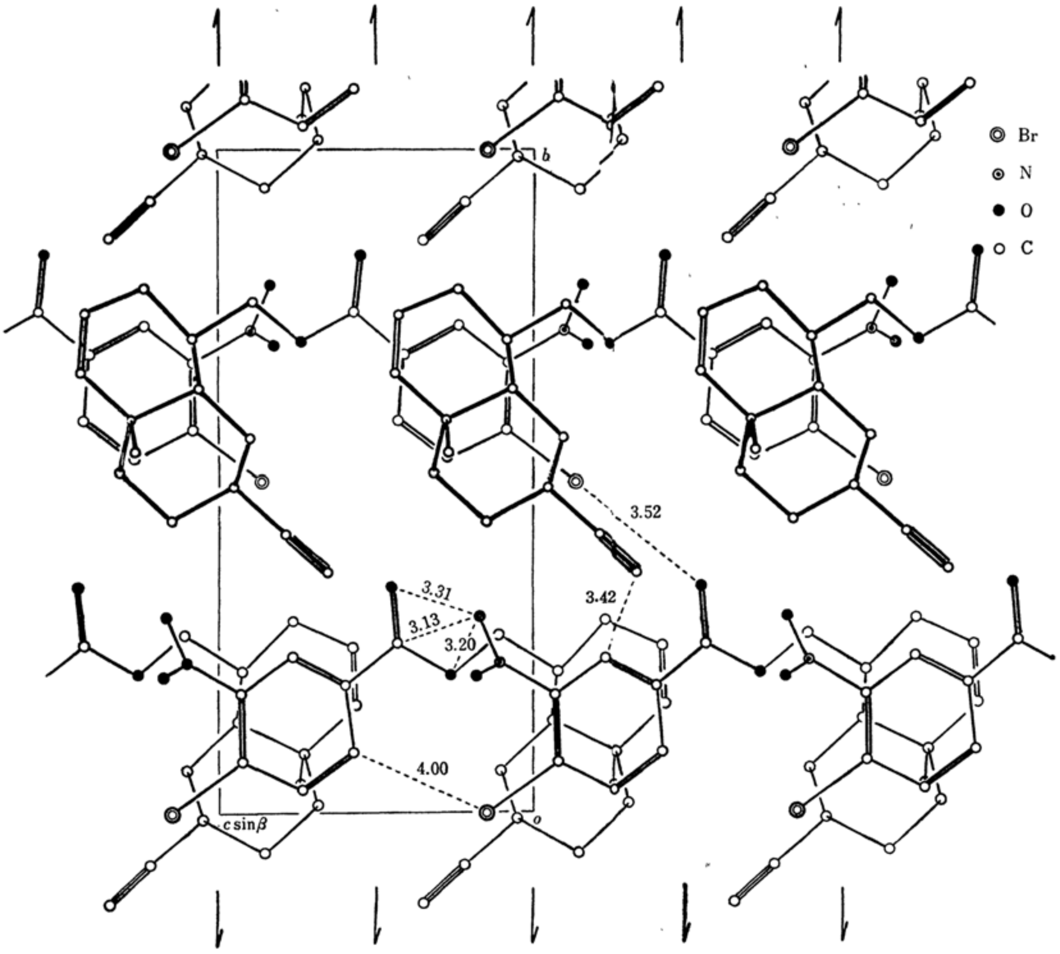

Fig. 9. The crystal structure projected along the a axis and the short intermolecular distances (Å).

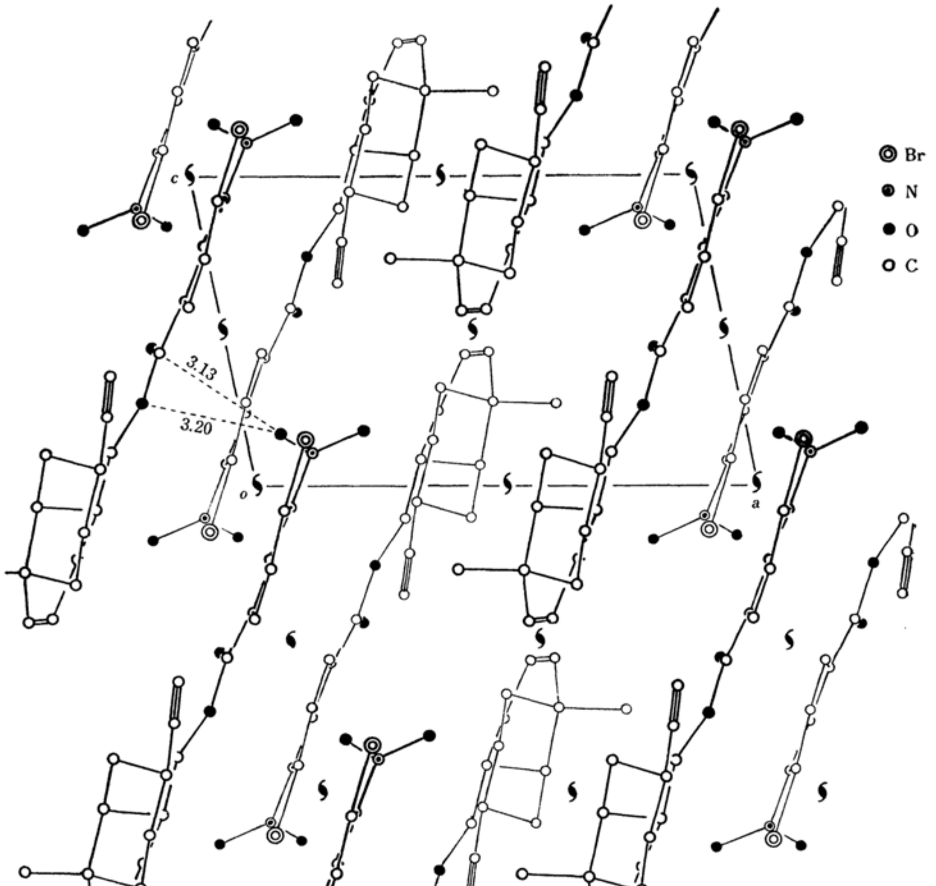

Fig. 10. The crystal structure projected along the b axis and the short intermolecular distances (Å).

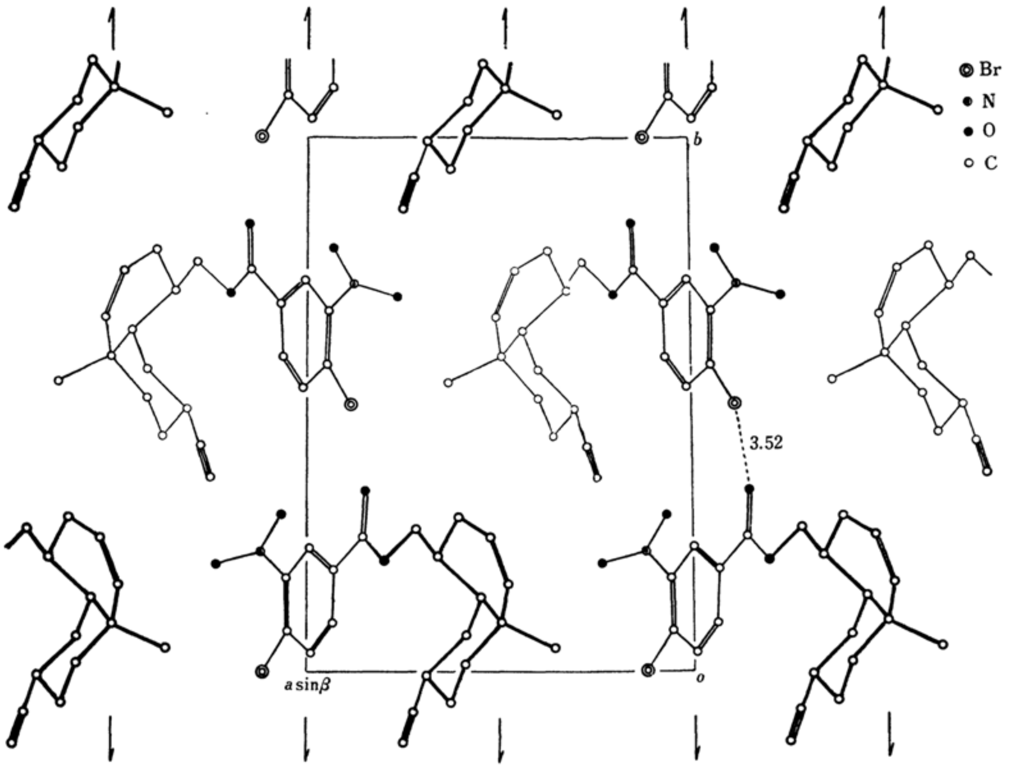

Fig. 11. The crystal structure projected along the c axis and the short intermolecular distances (Å).

ring assumes the chair form. It is indicated that no strain occurs in the ring system.

That the steroid conformation of the present compound is more favorable can be reasonably explained from the stereochemical point of view. If the molecule were forced to take the non-steroid form keeping the chair and the half-chair conformation of the two rings, strong 1,3-diaxial interaction between 4β-hydroxymethyl group and 10β-methyl group would occur as shown in Fig. 8(a). Alternatively, if 4β-hydroxymethyl group were in the equatorial position in order to avoid such 1,3-diaxial interaction, the ring A should be in the less stable half-boat conformation as shown in Fig. 8(b). Consequently, the steroid conformation of this compound is more stable than the non-steroid one. If 4-hydroxymethyl group is in the α orientation, the non-steroid conformation can occur favorably.

Crystal Structure. The packing diagrams of the crystal viewed along the a, b and c axes are shown in Figs. 9, 10 and 11, respectively, together with the short intermolecular distances. The strong dipolar nature of the C=O group may fix the orientation of the nitro group to give the shortest intermolecular carbon-oxygen distance (3.13 Å). The shortest carbon-carbon, oxygen-oxygen, bromine-carbon and bromine-oxygen distances are 3.42 Å, 3.20 Å, 4.00 Å and 3.52 Å, respectively. No unusual short approaches are observed.

The authors are indebted to Professor Kahei Takase and Dr. Toyonobu Asao of Tohoku University for kindly giving us the sample.