The Crystal and Molecular Structure of *p*-Bromophenacyl Retigerate A

By Rumiko Takahashi and Yoichi Iitaka

Faculty of Pharmaceutical Sciences, University of Tokyo, Hongo, Tokyo, Japan

The crystal structure of *p*-bromophenacyl retigerate A, $C_{38}H_{53}O_5Br$, has been determined in order to elucidate the molecular structure and absolute configuration of retigeric acid A, $C_{30}H_{48}O_4$, a triterpene isolated from a lichen, *Lobaria isidiosa*. The crystals are orthorhombic with space group $P2_12_12$ and the unit-cell dimensions are, $a = 20.66$, $b = 22.44$, $c = 7.40$ Å, $Z = 4$. The crystal structure was solved by the heavy-atom method and refined by the block-matrix least-squares method. The final R value for 1684 independent observed reflexions was 0.103. The absolute configuration was determined by the anomalous dispersion method. The molecular structure of retigeric acid A was formulated by the present analysis as 2α, 3β-dihydroxy fern-9(11)-en-23-oic acid which was found to be one of the fernane group triterpenes.

Introduction

Retigeric acid A, $C_{30}H_{48}O_4$, is one of the triterpenes which have been isolated from a lichen, *Lobaria isidiosa* collected in Bhutan, in the eastern Himalayas. On the basis of chemical and spectroscopic data, it was supposed that retigeric acid A is a pentacyclic triterpene having the chemical formula as indicated in Fig. 1 (I). However it was not possible to confirm the structure because of the limited amount of samples available for chemical investigation. The positions and configurations of the two hydroxyl groups in ring *A*, the location of the double bond in the skeleton of the molecule and the configuration of C(21) in ring *E* were open to suspicion. An X-ray structure analysis of *p*-bromophenacyl retigerate A, Fig. 1 (II), was therefore undertaken in order to establish the chemical structure and the stereochemistry of retigeric acid A including its absolute configuration.

Experimental

Retigeric acid A was treated with *p*-bromophenacyl bromide to give *p*-bromophenacyl retigerate A. The product was recrystallized from a mixed solution of ethyl acetate, ethanol and water. The crystals obtained

Fig. 1. Chemical formulae: (I) retigeric acid A, (II) *p*-bromophenacyl retigerate A.

were colourless prisms elongated along the *c* axis. The density was measured by the flotation method in a mixture of benzene and carbon tetrachloride. The cell dimensions and space group were determined from precession photographs of *h0l* and 0*kl* taken with Cu *Kα* radiation.

Crystal data

p-Bromophenacyl retigerate A, $C_{38}H_{53}O_5$ Br:
  M.W. 669·7, m.p. 245–247 °C
Orthorhombic
$a = 20.66 \pm 0.04$, $b = 22.44 \pm 0.05$, $c = 7.40 \pm 0.02$ Å;
$U = 3351$ Å^3;
$D_m = 1.30$ g.cm^{-3}, $D_x = 1.29$ g.cm^{-3}; $Z = 4$;
μ for Cu $K\alpha = 21.2$ cm^{-1};
$F(000) = 1424$.
Absent spectra: *h*00 when *h* is odd, 0*k*0 when *k* is odd. Space group $P2_12_12$.

The three-dimensional intensity data were collected from equi-inclination Weissenberg photographs. The layers *hk*0 to *hk*5 about the *c* axis and 0*kl* to 5*kl* about the *a* axis were taken with Cu *Kα* radiation using the multiple film technique. The intensities were measured on a Narumi microdensitometer. The specimens used for the intensity measurement were small enough to neglect the absorption correction. All the intensity data were then corrected for Lorentz and polarization factors and put on a common scale by correlating the structure factors on various layers. 1684 non-zero independent structure factors were finally derived. A Wilson plot was then made to estimate the approximate scale factor and overall temperature factor, the latter was found to be 4·5 Å^2.

Determination of the structure

The position of the bromine atom was easily derived from the three sharpened Patterson–Harker sections at $u = \frac{1}{2}$, $v = \frac{1}{2}$ and $w = 0$ respectively. The whole struc-
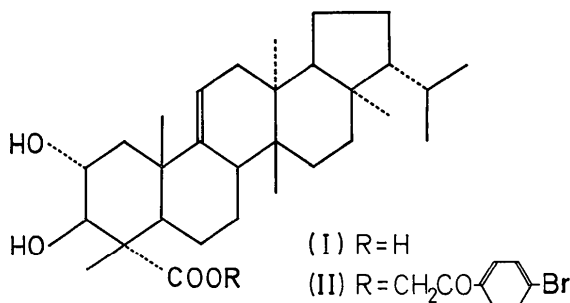
ture was revealed at the third Fourier synthesis, the R value at this stage being 0·20. The oxygen atoms were identified on the difference Fourier map with the help of chemical and structural considerations.

Refinement of the structural parameters was carried out by the block-matrix least-squares calculation using the program *HBLS* (Okaya & Ashida, 1967). Six cycles of calculation with anisotropic temperature factors for all atoms gave the R value of 0·103 for 1684 observed reflexions. The weighting functions used were,

$$\sqrt{w}=8/F_o \quad \text{when} \quad F_o>8 ,$$
$$\sqrt{w}=1 \quad \text{when} \quad F_o\le8 .$$

The following atomic scattering factors were used for the present structure determination: for oxygen and carbon, those of Berghuis, Haanappel, Potters, Loopstra, MacGillavry & Veenendaal (1955) and for bromine, those of Thomas & Umeda (1957). The final atomic parameters are presented in Table 1 along with their standard deviations. The observed and calculated structure factors are compared in Table 2. The final electron density map and the molecular structure are shown in Fig. 2.

The absolute configuration of the structure was determined by the anomalous dispersion method (Bijvoet, Peerdeman & van Bommel, 1951). The dispersion terms of the bromine scattering factor for Cu $K\alpha$ radiation were assumed to be $\Delta f'=-0\cdot9$ and $\Delta f''=1\cdot5$, according to Dauben & Templeton (1955). The intensities of the Friedel pairs of reflexions were calculated and compared with the observed values assuming the left-handed set of axes. Eleven pairs of hkl and $\overline{hkl}$ showed significant differences in the lth layer Weissenberg photographs. The result is shown in Table 3.

Table 1. *Final atomic parameters* ($\times 10^4$)

Temperature factors are expressed as
$$T=\exp\{-(\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\} .$$
The e.s.d.'s given in the parentheses denote the least significant digits.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Br	864 (1)	286 (1)	−8468 (4)	31 (1)	25 (0)	410 (7)	−4 (1)	−24 (2)	−11 (2)
C(1)	1235 (11)	4544 (10)	2365 (28)	32 (7)	32 (6)	114 (43)	−6 (5)	−9 (14)	18 (13)
C(2)	1459 (11)	3894 (9)	2728 (25)	39 (7)	20 (5)	102 (40)	−10 (5)	−5 (15)	28 (11)
C(3)	1561 (10)	3558 (9)	1024 (25)	28 (6)	23 (5)	138 (43)	−11 (5)	−9 (14)	33 (12)
C(4)	2036 (8)	3861 (8)	−263 (26)	14 (5)	20 (4)	160 (43)	−5 (4)	−31 (13)	22 (12)
C(5)	1845 (9)	4528 (7)	−572 (24)	21 (5)	12 (4)	107 (37)	−4 (4)	−2 (12)	14 (10)
C(6)	2251 (10)	4834 (8)	−2089 (32)	27 (6)	16 (5)	347 (64)	5 (4)	21 (17)	64 (14)
C(7)	2233 (8)	5509 (8)	−1952 (27)	16 (5)	17 (4)	200 (48)	−4 (3)	34 (13)	20 (11)
C(8)	1570 (8)	5706 (6)	−1291 (23)	15 (4)	10 (3)	93 (34)	−2 (3)	15 (11)	8 (9)
C(9)	1441 (10)	5500 (7)	575 (26)	27 (6)	14 (4)	150 (43)	−3 (4)	−11 (14)	21 (11)
C(10)	1744 (8)	4891 (8)	1135 (22)	14 (4)	22 (5)	72 (34)	−4 (4)	−19 (11)	16 (10)
C(11)	1096 (12)	5815 (10)	1782 (28)	43 (8)	31 (5)	111 (42)	3 (6)	26 (16)	2 (13)
C(12)	758 (10)	6414 (9)	1363 (28)	30 (6)	22 (5)	171 (46)	−1 (5)	−3 (16)	10 (13)
C(13)	781 (9)	6547 (8)	−663 (22)	17 (5)	19 (4)	72 (35)	−4 (4)	13 (11)	3 (10)
C(14)	1467 (8)	6405 (7)	−1453 (23)	17 (4)	12 (3)	97 (35)	−4 (3)	−15 (12)	2 (10)
C(15)	1515 (8)	6611 (7)	−3466 (25)	17 (5)	17 (4)	114 (37)	−3 (4)	32 (13)	4 (11)
C(16)	1358 (8)	7276 (7)	−3699 (26)	17 (5)	13 (4)	174 (43)	5 (3)	32 (13)	14 (11)
C(17)	686 (8)	7463 (8)	−2911 (26)	11 (4)	16 (4)	171 (44)	−5 (4)	4 (11)	7 (11)
C(18)	653 (8)	7231 (8)	−916 (23)	11 (4)	19 (4)	120 (41)	−2 (3)	11 (11)	−16 (10)
C(19)	51 (10)	7521 (9)	−197 (26)	31 (6)	20 (4)	125 (39)	11 (5)	26 (15)	−8 (12)
C(20)	104 (10)	8165 (9)	−1002 (30)	23 (6)	25 (5)	236 (55)	2 (5)	−2 (16)	24 (15)
C(21)	622 (8)	8149 (8)	−2436 (27)	12 (4)	19 (4)	185 (44)	1 (4)	−13 (12)	−23 (12)
C(22)	475 (9)	8596 (8)	−3949 (30)	23 (6)	16 (4)	244 (55)	2 (4)	1 (15)	10 (12)
C(23)	1914 (8)	3551 (7)	−2019 (24)	13 (4)	16 (4)	142 (40)	1 (3)	10 (12)	20 (10)
C(24)	2778 (10)	3785 (9)	307 (34)	25 (6)	23 (5)	290 (60)	−1 (5)	−28 (17)	7 (16)
C(25)	2348 (10)	5029 (9)	2235 (25)	32 (7)	22 (4)	132 (40)	−13 (5)	−35 (14)	5 (12)
C(26)	2013 (8)	6702 (8)	−350 (28)	11 (5)	18 (4)	219 (46)	2 (4)	−34 (13)	−22 (12)
C(27)	245 (8)	6151 (8)	−1487 (31)	8 (4)	24 (5)	256 (51)	−5 (4)	6 (14)	−5 (15)
C(28)	149 (10)	7296 (9)	−4219 (25)	22 (6)	32 (6)	115 (42)	−2 (5)	−38 (13)	11 (13)
C(29)	1002 (15)	8573 (12)	−5503 (42)	56 (11)	35 (7)	361 (76)	7 (8)	8 (25)	37 (21)
C(30)	431 (12)	9206 (9)	−3240 (45)	39 (8)	15 (4)	507 (88)	4 (5)	14 (5)	−14 (19)
C(31)	2129 (10)	2726 (8)	−3848 (26)	27 (6)	19 (4)	134 (42)	−6 (4)	15 (14)	6 (12)
C(32)	1728 (8)	2190 (8)	−3049 (26)	16 (5)	17 (4)	180 (47)	0 (4)	5 (13)	28 (11)
C(33)	1517 (9)	1742 (7)	−4400 (26)	20 (5)	12 (4)	175 (44)	−2 (4)	−3 (13)	13 (11)
C(34)	1452 (10)	1148 (9)	−3784 (30)	23 (6)	27 (5)	217 (5)	0 (5)	−1 (16)	22 (15)
C(35)	1241 (10)	715 (8)	−5056 (30)	27 (6)	16 (5)	238 (55)	3 (4)	17 (16)	31 (13)
C(36)	1129 (10)	880 (8)	−6735 (34)	24 (6)	17 (4)	280 (57)	−3 (4)	−15 (17)	−5 (14)
C(37)	1160 (10)	1467 (8)	−7422 (33)	22 (5)	14 (4)	325 (61)	−2 (4)	24 (16)	4 (14)
C(38)	1390 (11)	1877 (9)	−6146 (32)	34 (7)	23 (5)	256 (59)	−1 (5)	−6 (19)	29 (15)
O(1)	914 (7)	3619 (7)	3665 (19)	33 (4)	41 (4)	182 (33)	−24 (4)	−31 (12)	50 (10)
O(2)	1790 (7)	2973 (6)	1521 (19)	43 (5)	24 (3)	150 (3)	−3 (3)	−21 (11)	35 (9)
O(3)	1435 (7)	3611 (6)	−2943 (18)	39 (5)	22 (3)	174 (33)	2 (3)	−40 (11)	0 (8)
O(4)	2329 (6)	3101 (6)	−2425 (20)	23 (4)	21 (3)	274 (37)	−1 (3)	17 (10)	18 (9)
O(5)	1607 (6)	2166 (6)	−1463 (20)	23 (4)	35 (4)	190 (32)	−1 (3)	−6 (10)	30 (11)

A comparison between the observed and calculated intensities indicated that the assumed configuration was actually the antipode of the true structure. The absolute configuration was therefore established as shown in Fig. 1 (II). All Figures presented in this paper are drawn with the correct absolute configuration.

Discussion of the structure

The molecular structure

The present structure determination of *p*-bromophenacyl retigerate A firmly established the structure of retigeric acid A as shown in Fig. 1 (I) in accordance

Table 2. *Observed and calculated structure factors*

H	K	L	|F(OBS)|	|F(CAL)|
2	0	0	42.55	44.54
4	0	0	171.96	236.16
8	0	0	34.32	11.12
12	0	0	65.10	72.43
14	0	0	66.08	68.13
16	0	0	35.76	36.29
18	0	0	25.30	21.56
1	1	0	19.34	26.85
2	1	0	56.54	79.37
3	1	0	145.59	164.71
4	1	0	169.82	217.96
5	1	0	153.73	183.03
6	1	0	90.49	87.57
7	1	0	60.26	53.30
8	1	0	16.41	6.78
9	1	0	15.30	16.11
10	1	0	16.37	13.70
11	1	0	57.52	55.50
12	1	0	13.53	18.56
14	1	0	11.05	15.94
16	1	0	28.88	30.04
17	1	0	12.28	14.40
18	1	0	16.74	17.26
20	1	0	16.09	18.13
23	1	0	17.67	19.53
0	2	0	40.46	23.87
1	2	0	22.32	21.18
2	2	0	43.90	26.02
3	2	0	113.41	133.57
4	2	0	65.66	68.78
5	2	0	82.40	83.59
6	2	0	145.31	146.54
7	2	0	53.75	63.65
8	2	0	12.37	8.27
9	2	0	31.95	22.38
10	2	0	48.45	53.08
11	2	0	18.74	23.52
12	2	0	14.46	16.77
14	2	0	28.97	27.66
15	2	0	38.73	40.26
16	2	0	34.97	37.04
18	2	0	22.88	23.55
22	2	0	22.32	24.84
1	3	0	92.16	97.14
2	3	0	83.79	91.63
3	3	0	21.39	18.61
4	3	0	88.16	101.77
5	3	0	73.14	86.72
6	3	0	80.58	66.95
7	3	0	97.98	97.47
8	3	0	55.66	55.48
10	3	0	32.46	26.17
11	3	0	71.05	78.53
12	3	0	19.55	18.39
13	3	0	33.01	37.15
14	3	0	26.94	21.02
15	3	0	15.07	14.02
16	3	0	44.55	44.23
17	3	0	60.26	66.19
18	3	0	25.48	21.33
19	3	0	24.37	24.58
0	4	0	38.04	31.19
1	4	0	48.45	51.84
3	4	0	49.57	45.62
4	4	0	86.35	87.67
5	4	0	75.00	74.79
6	4	0	57.75	56.42
7	4	0	92.58	83.44
8	4	0	38.97	35.32
9	4	0	41.48	40.33
10	4	0	36.78	37.77
12	4	0	64.26	73.11
13	4	0	35.06	33.30
15	4	0	16.27	20.32
17	4	0	16.46	8.81
18	4	0	24.78	19.29
20	4	0	26.32	26.74
22	4	0	19.20	18.03
1	5	0	67.75	73.10
2	5	0	59.66	50.78
3	5	0	24.60	12.87
4	5	0	71.98	74.88
5	5	0	85.56	85.99
6	5	0	46.64	37.20
7	5	0	37.99	33.63
8	5	0	84.86	82.41
9	5	0	43.99	39.41
10	5	0	59.19	58.82
11	5	0	64.17	63.89
12	5	0	31.09	33.53
13	5	0	31.02	31.78
14	5	0	20.13	22.43
17	5	0	47.60	47.74
20	5	0	17.39	14.70
22	5	0	16.83	20.56
0	6	0	91.98	101.89
1	6	0	106.39	112.73
2	6	0	57.89	52.18
3	6	0	109.37	121.55
4	6	0	31.71	28.88
5	6	0	23.06	19.79
6	6	0	68.26	59.74
7	6	0	42.22	37.44
8	6	0	30.36	31.41
9	6	0	53.06	48.33
11	6	0	37.80	38.48
12	6	0	45.66	48.64
15	6	0	49.52	53.63
16	6	0	25.30	21.22
18	6	0	20.51	18.74
19	6	0	24.55	24.23
1	7	0	18.18	15.91
2	7	0	89.79	92.22
3	7	0	49.20	49.02
4	7	0	87.51	84.43
5	7	0	23.76	25.69
7	7	0	43.62	38.79
8	7	0	49.20	51.43
9	7	0	43.15	44.33
10	7	0	35.15	32.89
12	7	0	19.11	22.18
14	7	0	47.01	47.45
18	7	0	17.25	17.35
20	7	0	23.62	22.44
0	8	0	61.47	56.05
1	8	0	12.18	12.02
2	8	0	30.36	31.08
3	8	0	31.34	32.11
4	8	0	14.83	9.72
5	8	0	25.42	20.29
6	8	0	24.15	27.34
7	8	0	51.66	48.85
9	8	0	77.19	76.17
10	8	0	18.00	16.88
11	8	0	28.23	17.95
12	8	0	18.09	17.61
14	8	0	13.21	14.07
15	8	0	49.34	55.50
16	8	0	19.05	15.35
19	8	0	30.13	30.89
1	9	0	43.20	30.79
2	9	0	67.66	64.78
3	9	0	84.33	65.28
4	9	0	60.73	51.25
7	9	0	19.48	13.35
8	9	0	57.71	58.38
9	9	0	11.11	13.57
10	9	0	48.59	47.25
12	9	0	37.20	36.09
14	9	0	23.39	24.66
16	9	0	16.88	15.29
18	9	0	19.72	18.50
19	9	0	17.34	19.30
0	10	0	100.77	78.73
1	10	0	38.04	29.13
2	10	0	56.50	49.23
3	10	0	100.72	95.47
4	10	0	73.01	65.62
5	10	0	69.24	76.49
6	10	0	29.53	18.97
9	10	0	38.14	33.38
10	10	0	18.60	14.14
11	10	0	34.15	[illegible]
13	10	0	40.08	43.16
14	10	0	28.23	28.97
15	10	0	24.51	22.44
17	10	0	21.72	19.82
18	10	0	14.49	12.40
1	11	0	65.47	58.86
2	11	0	135.83	132.57
3	11	0	25.25	23.10
4	11	0	17.11	14.44
6	11	0	13.90	14.15
7	11	0	50.31	46.48
8	11	0	34.60	34.80
10	11	0	56.26	61.33
11	11	0	25.76	22.75
12	11	0	17.81	17.34
14	11	0	43.09	42.08
15	11	0	40.13	38.44
16	11	0	23.53	25.55
18	11	0	14.65	15.55
0	12	0	51.99	53.38
1	12	0	32.30	[illegible]
2	12	0	23.27	17.98
3	12	0	57.75	51.39
4	12	0	32.97	28.26
5	12	0	16.32	12.83
6	12	0	13.67	10.75
7	12	0	19.11	23.44
8	12	0	30.32	29.19
9	12	0	44.50	44.30
11	12	0	21.60	21.11
12	12	0	19.30	17.76
13	12	0	26.55	25.47
16	12	0	17.34	17.10
18	12	0	15.95	17.54
19	12	0	31.93	36.93
1	13	0	61.94	[illegible]
2	13	0	23.34	22.11
3	13	0	11.49	10.00
4	13	0	51.85	46.18
5	13	0	49.06	41.46
6	13	0	15.30	13.84
7	13	0	28.23	26.87
8	13	0	43.94	38.33
11	13	0	21.20	22.89
12	13	0	16.55	17.26
13	13	0	48.22	54.54
14	13	0	27.53	29.19
15	13	0	17.34	15.21
17	13	0	19.52	21.95
18	13	0	17.02	12.34
0	14	0	7.25	6.75
1	14	0	59.06	55.82
2	14	0	28.97	30.45
3	14	0	55.10	55.61
4	14	0	30.69	28.08
6	14	0	43.11	35.55
7	14	0	27.11	22.13
9	14	0	34.60	35.87
10	14	0	26.83	29.10
12	14	0	16.93	16.51
13	14	0	15.93	10.07
14	14	0	27.81	27.53
18	14	0	19.95	18.11
1	15	0	31.06	31.58
2	15	0	24.78	23.97
3	15	0	26.60	24.59
5	15	0	34.07	32.30
7	15	0	18.97	19.12
8	15	0	25.20	23.14
11	15	0	37.43	38.27
12	15	0	25.16	23.35
13	15	0	34.69	37.78
14	15	0	17.39	17.07
15	15	0	24.51	25.33
0	16	0	29.16	27.43
1	16	0	19.90	17.13
2	16	0	22.74	23.31
3	16	0	4.79	12.38
4	16	0	52.50	53.02
6	16	0	32.97	32.72
7	16	0	35.67	32.95
8	16	0	29.53	26.86
9	16	0	18.74	17.55
10	16	0	28.13	29.33
12	16	0	19.67	19.66
14	16	0	14.65	9.98
1	17	0	38.55	38.51
3	17	0	3.53	6.40
4	17	0	3.81	4.78
5	17	0	25.85	25.70
6	17	0	14.14	14.19
7	17	0	36.64	35.75
9	17	0	19.48	19.20
10	17	0	17.30	17.16
0	18	0	43.06	40.84
2	18	0	43.80	44.74
4	18	0	30.36	27.03
5	18	0	36.13	32.51
6	18	0	47.99	50.26
10	18	0	20.79	19.30
12	18	0	21.62	22.51
1	19	0	44.41	44.07
5	19	0	20.13	18.51
7	19	0	20.79	20.54
0	20	0	24.09	20.90
2	20	0	14.23	13.73
4	20	0	3.21	11.79
6	20	0	17.39	15.84
9	20	0	14.51	14.66
1	21	0	21.39	21.45
3	21	0	26.50	25.14
4	21	0	4.28	12.80
5	21	0	18.69	12.60
1	22	0	24.97	25.13
4	23	0	20.04	22.93
5	23	0	15.72	15.64
0	24	0	15.81	18.53
3	24	0	19.30	22.02
4	24	0	10.14	11.01
0	0	1	143.31	176.08
1	0	1	23.62	8.94
2	0	1	59.27	41.46
3	0	1	18.00	5.29
4	0	1	68.82	59.90
5	0	1	188.28	229.50
6	0	1	15.48	6.55
7	0	1	41.38	13.16
8	0	1	81.61	84.24
9	0	1	63.94	62.73
10	0	1	60.31	56.34
11	0	1	135.93	[illegible]
12	0	1	68.31	65.80
13	0	1	28.78	26.06
14	0	1	20.65	13.74
15	0	1	17.72	19.84
17	0	1	15.21	13.95
0	1	1	73.91	92.42
1	1	1	75.89	72.03
2	1	1	45.43	47.56
3	1	1	150.89	188.07
4	1	1	37.69	23.76
5	1	1	56.96	69.82
6	1	1	68.54	72.94
7	1	1	62.08	52.54
8	1	1	36.74	23.61
9	1	1	40.07	32.91
10	1	1	54.50	55.68
11	1	1	45.06	41.48
12	1	1	36.69	37.40
13	1	1	33.01	30.24
14	1	1	23.11	12.61
15	1	1	15.34	16.27
16	1	1	30.04	35.32
17	1	1	20.46	20.74
18	1	1	19.90	23.55
0	2	1	93.05	112.57
1	2	1	143.06	183.36
2	2	1	43.66	37.31
3	2	1	112.39	118.46
4	2	1	97.98	[illegible]
5	2	1	105.88	113.50
6	2	1	52.36	48.08
7	2	1	56.26	49.10
8	2	1	83.10	77.53
9	2	1	51.52	41.67
10	2	1	18.46	16.59
11	2	1	45.15	41.09
12	2	1	30.92	23.35
13	2	1	51.64	55.10
14	2	1	25.48	27.34
15	2	1	18.93	15.96
16	2	1	35.43	29.57
18	2	1	22.27	23.73
19	2	1	17.62	17.25
0	3	1	39.43	42.45
1	3	1	105.79	113.50
2	3	1	80.16	92.33
3	3	1	42.38	35.63
4	3	1	42.59	32.99
5	3	1	75.42	72.73
6	3	1	90.21	93.33
7	3	1	69.33	61.79
8	3	1	94.44	92.47
9	3	1	24.91	18.40
10	3	1	59.57	51.13
11	3	1	30.46	26.37
12	3	1	63.80	68.58
13	3	1	34.04	32.41
15	3	1	19.00	23.36
16	3	1	28.88	26.45
17	3	1	39.48	40.15
0	4	1	57.57	64.66
1	4	1	38.64	33.86
2	4	1	97.51	110.34
3	4	1	45.57	39.70
4	4	1	93.56	81.88
5	4	1	32.41	26.45
6	4	1	35.62	37.33
7	4	1	16.41	7.55
8	4	1	14.51	10.75
9	4	1	46.36	39.26
10	4	1	67.84	66.51
11	4	1	28.23	29.04
12	4	1	53.10	53.42
13	4	1	24.74	24.86
14	4	1	33.01	30.82
15	4	1	34.55	32.93
17	4	1	30.92	33.00
18	4	1	20.09	15.50
19	4	1	17.67	17.67
20	4	1	14.51	11.60
22	4	1	19.86	17.58
0	5	1	59.68	47.46
1	5	1	84.49	84.42
2	5	1	62.45	64.69
3	5	1	78.21	63.95
4	5	1	39.15	40.53
5	5	1	58.68	57.09
6	5	1	102.39	[illegible]
7	5	1	43.09	39.75
8	5	1	39.76	36.54
9	5	1	60.12	54.63
10	5	1	44.22	41.18
11	5	1	20.04	18.48
14	5	1	46.96	43.88
15	5	1	15.90	17.47
16	5	1	30.92	33.21
17	5	1	33.43	32.54
18	5	1	24.74	23.64
20	5	1	14.51	18.68
22	5	1	19.72	17.45
0	6	1	58.92	51.01
1	6	1	65.66	58.15
2	6	1	34.74	23.63
3	6	1	31.76	22.38
4	6	1	93.01	89.92
5	6	1	35.43	28.27
6	6	1	42.13	33.86
7	6	1	45.29	45.00
8	6	1	64.68	63.75
9	6	1	42.30	36.72
10	6	1	31.76	31.06
11	6	1	39.62	38.51
12	6	1	14.14	9.89
13	6	1	18.18	21.36
14	6	1	44.31	45.04
15	6	1	31.62	31.97
16	6	1	[illegible]	[illegible]
17	6	1	19.90	17.28
18	6	1	18.97	17.50
20	6	1	22.88	22.49
0	7	1	59.57	52.51
1	7	1	42.55	41.25
2	7	1	43.13	38.69
3	7	1	87.51	89.64
4	7	1	79.38	72.51
5	7	1	43.66	38.77
6	7	1	45.24	41.76
7	7	1	33.27	27.14
8	7	1	41.29	41.14
9	7	1	61.71	61.55
10	7	1	37.39	33.41
11	7	1	12.65	11.46
12	7	1	18.74	15.90
13	7	1	17.48	16.97
14	7	1	32.22	31.50
15	7	1	21.16	21.82
0	8	1	6.42	6.09
1	8	1	42.08	41.15
2	8	1	90.86	91.98
3	8	1	77.56	79.05
4	8	1	32.55	27.02
5	8	1	37.01	29.36
6	8	1	17.58	11.81
7	8	1	66.45	68.65
8	8	1	20.46	19.24
9	8	1	39.25	40.57
10	8	1	53.52	53.94
11	8	1	17.48	17.37
13	8	1	22.83	25.40
14	8	1	19.72	25.57
15	8	1	29.67	31.68
16	8	1	24.23	22.94
17	8	1	17.53	15.42
20	8	1	14.37	16.81
0	9	1	46.31	42.78
1	9	1	43.85	44.41
2	9	1	108.76	96.06
3	9	1	93.42	88.04
4	9	1	35.53	29.52
5	9	1	30.14	34.85
6	9	1	37.39	36.15
7	9	1	67.15	64.35
8	9	1	19.25	20.57
9	9	1	42.64	38.37
10	9	1	27.11	21.43
11	9	1	25.53	26.37
12	9	1	31.00	30.93
13	9	1	32.46	33.99
15	9	1	24.92	28.52
0	10	1	24.18	18.43
1	10	1	15.91	16.30
2	10	1	14.55	5.72
3	10	1	93.56	97.80
4	10	1	35.01	28.55
5	10	1	39.11	37.02
6	10	1	11.67	8.40
7	10	1	41.01	41.21
8	10	1	61.10	66.27
9	10	1	29.48	24.93
10	10	1	26.13	24.37
11	10	1	23.25	22.73
12	10	1	14.37	12.86
13	10	1	16.27	14.54
14	10	1	29.85	28.21
15	10	1	23.30	21.07
18	10	1	20.51	23.17
0	11	1	65.33	58.11
1	11	1	12.93	11.95
2	11	1	59.08	58.42
3	11	1	58.87	54.84
5	11	1	17.62	15.12
6	11	1	15.53	11.97
7	11	1	13.81	15.22
8	11	1	41.99	37.09
9	11	1	51.01	51.84
10	11	1	23.25	23.82
12	11	1	18.69	16.35
13	11	1	27.25	29.28
14	11	1	22.09	22.13
15	11	1	18.83	11.65
17	11	1	21.76	22.60
0	12	1	46.64	45.57
1	12	1	45.11	41.30
2	12	1	52.08	52.54
3	12	1	19.80	17.70
4	12	1	43.76	44.53
5	12	1	35.01	33.34
7	12	1	31.29	27.54
8	12	1	47.85	45.17
9	12	1	23.39	21.74
10	12	1	23.20	19.98
11	12	1	21.95	24.57
12	12	1	22.51	20.87
13	12	1	25.06	27.65
14	12	1	40.13	43.76
15	12	1	19.16	15.25
17	12	1	16.18	18.54
1	13	1	36.55	36.19
2	13	1	17.72	19.87
3	13	1	57.15	[illegible]
4	13	1	43.60	41.47
5	13	1	44.17	41.57
6	13	1	47.15	49.55
7	13	1	38.18	35.34
8	13	1	31.62	31.20
9	13	1	33.06	32.67
10	13	1	22.54	21.15
12	13	1	24.19	24.72
13	13	1	20.34	21.11
14	13	1	25.93	25.43
0	14	1	37.07	33.58
1	14	1	36.78	31.95
2	14	1	37.90	35.22
3	14	1	24.74	25.24
4	14	1	24.97	22.41
5	14	1	26.37	26.37
6	14	1	30.27	25.20
7	14	1	14.37	9.51
8	14	1	34.74	35.97
9	14	1	39.66	41.97
10	14	1	41.62	42.52
11	14	1	25.16	12.40
12	14	1	17.39	19.06
17	14	1	15.90	21.46
0	15	1	53.38	52.11
1	15	1	43.34	38.31
2	15	1	36.13	32.99
3	15	1	26.18	26.28
4	15	1	4.18	8.81
5	15	1	20.88	21.45
6	15	1	42.08	43.78
7	15	1	17.67	19.57
8	15	1	33.29	33.77
10	15	1	21.06	21.98
12	15	1	22.74	25.18
14	15	1	23.51	19.40
0	16	1	17.90	11.89
1	16	1	37.71	37.12
2	16	1	38.92	38.79
3	16	1	31.76	28.34
4	16	1	40.94	37.14
5	16	1	37.25	[illegible]
6	16	1	33.39	[illegible]
7	16	1	33.81	31.15
8	16	1	27.06	25.62
10	16	1	21.48	23.44
12	16	1	17.76	17.75
0	17	1	31.06	34.01
2	17	1	6.60	9.83
3	17	1	25.48	22.37
4	17	1	31.48	31.84
5	17	1	6.60	15.66
6	17	1	28.92	30.66
7	17	1	27.43	25.95
8	17	1	14.28	8.93
12	17	1	17.76	17.00
1	18	1	34.41	29.88
2	18	1	7.44	10.75
3	18	1	20.97	18.02
5	18	1	26.41	28.24
4	18	1	14.97	15.66
7	18	1	19.06	18.63
8	18	1	16.18	12.93
11	18	1	25.06	29.72
12	18	1	22.60	23.45
0	19	1	31.76	34.00
1	19	1	22.09	21.24
2	19	1	6.93	12.24
3	19	1	15.30	10.74
4	19	1	21.02	22.22
5	19	1	11.53	3.64
6	19	1	17.76	16.70
7	19	1	19.20	21.44
12	19	1	15.67	17.16
1	20	1	5.86	11.45
2	20	1	32.41	33.54
3	20	1	9.21	13.75
5	20	1	6.60	16.83
6	20	1	21.76	23.57
7	20	1	25.02	24.30
1	21	1	5.35	8.63
2	21	1	17.76	18.98
3	21	1	13.58	13.41
4	21	1	19.44	18.72
5	21	1	17.58	19.68
6	21	1	18.93	18.66
4	22	1	18.18	16.91
0	23	1	20.27	22.06
1	23	1	16.83	12.88
5	23	1	11.35	9.30
5	24	1	17.02	11.60
3	25	1	14.74	18.26
0	0	2	112.62	117.79
1	0	2	74.91	82.80
2	0	2	36.27	31.88
3	0	2	39.25	43.50
4	0	2	56.31	48.62
5	0	2	60.59	64.53
6	0	2	82.68	77.24
7	0	2	16.69	19.35
8	0	2	14.60	7.50
9	0	2	42.13	37.11
10	0	2	49.99	39.91
11	0	2	31.99	30.04
12	0	2	16.97	18.77
13	0	2	21.34	23.83
17	0	2	27.53	21.54
0	1	2	92.07	112.81
1	1	2	27.43	29.45
2	1	2	69.01	75.78
3	1	2	60.91	56.87
4	1	2	42.18	35.62
5	1	2	29.16	23.77
6	1	2	79.38	85.77
7	1	2	46.36	44.55
8	1	2	59.50	50.70
9	1	2	54.87	48.49
10	1	2	38.64	36.97
11	1	2	67.05	56.18
12	1	2	37.06	38.74
13	1	2	14.65	10.22
14	1	2	20.41	20.71
15	1	2	21.39	22.63
16	1	2	30.92	35.23
18	1	2	28.23	31.53
0	2	2	67.33	45.42
1	2	2	67.19	80.38
2	2	2	46.59	41.99
3	2	2	29.06	26.23
4	2	2	57.24	49.61
5	2	2	98.63	[illegible]
6	2	2	51.94	45.95
7	2	2	52.06	43.07
8	2	2	85.93	77.49
9	2	2	29.67	27.08
10	2	2	43.48	38.76
11	2	2	59.19	57.76
12	2	2	23.70	17.20
13	2	2	38.32	32.63
14	2	2	23.25	24.18
16	2	2	21.53	21.00
17	2	2	30.22	25.47
19	2	2	12.83	12.01
0	3	2	109.37	97.18
1	3	2	33.90	35.24
2	3	2	31.39	30.03
3	3	2	41.80	43.48
4	3	2	60.26	56.58
5	3	2	36.55	35.23
6	3	2	54.54	49.18
7	3	2	36.78	31.46
8	3	2	26.32	16.75
9	3	2	40.59	36.94
10	3	2	35.94	29.11
11	3	2	37.25	33.66
12	3	2	45.80	48.84
13	3	2	31.62	28.19
14	3	2	19.16	17.84
15	3	2	46.96	46.49
16	3	2	26.18	24.32
17	3	2	20.55	17.74
19	3	2	14.37	13.87
21	3	2	15.48	16.35
0	4	2	38.78	32.74
1	4	2	86.54	97.52
2	4	2	85.23	83.68
3	4	2	28.78	29.44
4	4	2	34.69	28.69
5	4	2	62.45	65.93
6	4	2	84.82	78.54
7	4	2	53.80	54.99
8	4	2	55.89	56.56
9	4	2	66.03	68.12
10	4	2	47.29	47.88
11	4	2	63.66	62.88
12	4	2	18.97	13.79
16	4	2	20.97	22.90
17	4	2	18.69	25.48
19	4	2	21.30	22.00
20	4	2	23.27	16.65
0	5	2	60.54	53.19
1	5	2	50.73	49.50
2	5	2	39.66	39.45
3	5	2	44.31	40.16
4	5	2	38.32	35.11
5	5	2	81.75	81.03
6	5	2	121.18	122.02
7	5	2	35.20	38.74
8	5	2	34.41	32.01
9	5	2	93.84	90.25
10	5	2	45.20	45.69
11	5	2	24.60	25.15
12	5	2	17.90	17.13
13	5	2	23.02	19.79
14	5	2	23.39	22.68
15	5	2	17.72	17.17
0	6	2	44.78	45.28
1	6	2	35.62	25.73
2	6	2	32.64	32.30
3	6	2	43.11	35.73
4	6	2	72.17	82.05
5	6	2	33.67	29.28
6	6	2	31.67	25.36
7	6	2	30.18	23.19
8	6	2	26.69	23.04
9	6	2	52.59	49.97
11	6	2	31.93	31.86
12	6	2	19.06	17.72
13	6	2	27.62	28.84
14	6	2	27.02	26.29
15	6	2	23.16	27.81
16	6	2	19.48	21.73
0	7	2	86.45	73.05
1	7	2	48.22	43.38
2	7	2	34.64	32.00
3	7	2	83.42	83.69
4	7	2	37.01	32.58
5	7	2	55.99	55.15
6	7	2	28.13	23.05
7	7	2	34.13	34.65
8	7	2	46.83	45.82
9	7	2	78.45	74.42
10	7	2	38.97	39.74
13	7	2	32.02	32.38
15	7	2	23.48	23.58
16	7	2	15.25	17.49
0	8	2	13.02	5.42
1	8	2	33.39	26.74
2	8	2	86.16	82.07
3	8	2	41.34	35.39
4	8	2	65.15	69.30
5	8	2	29.39	26.19
6	8	2	28.69	20.81
7	8	2	21.58	16.51
8	8	2	57.52	59.41
10	8	2	48.78	48.60
11	8	2	10.65	13.97
12	8	2	20.04	19.20
14	8	2	35.80	35.41
16	8	2	14.09	9.23
18	8	2	21.34	22.81
0	9	2	38.55	32.93
1	9	2	35.25	36.78
2	9	2	72.03	71.44
3	9	2	65.84	65.12
4	9	2	43.34	41.08
5	9	2	3.16	5.98
6	9	2	27.34	24.27
7	9	2	54.40	56.54
8	9	2	20.18	20.24
9	9	2	16.09	15.52
13	9	2	15.58	19.11
15	9	2	24.92	24.67
19	9	2	15.58	14.30
0	10	2	33.96	27.42
1	10	2	58.82	52.01
2	10	2	55.43	56.36
3	10	2	33.04	26.78
4	10	2	61.94	57.14
5	10	2	34.07	31.48
6	10	2	17.25	15.19
8	10	2	57.38	63.48
9	10	2	25.90	28.81
10	10	2	25.11	24.21
11	10	2	27.16	23.25
12	10	2	24.13	20.97
13	10	2	19.99	20.06
14	10	2	23.11	23.43
16	10	2	18.09	[illegible]
20	10	2	16.14	19.55
0	11	2	37.62	29.48
1	11	2	35.06	36.78
2	11	2	48.59	41.47
3	11	2	67.05	63.41
4	11	2	4.37	9.54
5	11	2	21.39	24.42
6	11	2	36.27	34.55
7	11	2	15.53	13.06
8	11	2	25.53	24.73
9	11	2	36.83	35.31
10	11	2	24.69	25.14
12	11	2	31.76	34.18
13	11	2	28.83	31.55
14	11	2	25.11	26.18
0	12	2	14.97	12.57
1	12	2	29.20	21.64
2	12	2	44.50	42.67
3	12	2	26.55	25.97
4	12	2	29.34	25.35
5	12	2	30.88	25.27
6	12	2	22.37	22.42
7	12	2	12.09	13.20
8	12	2	23.53	19.65
9	12	2	22.78	21.50
10	12	2	13.07	13.63
11	12	2	18.97	19.96
12	12	2	30.09	30.60
14	12	2	28.41	26.63
17	12	2	15.62	16.53
18	12	2	16.55	18.06
0	13	2	50.96	50.18
2	13	2	19.81	17.21
3	13	2	38.18	39.14
4	13	2	25.95	24.10
5	13	2	27.43	25.83
6	13	2	23.30	22.00
7	13	2	17.81	14.75
8	13	2	27.02	27.45
9	13	2	37.25	37.76
10	13	2	18.04	17.63
12	13	2	18.79	20.78
13	13	2	17.95	[illegible]
15	13	2	12.88	14.03
1	14	2	23.44	21.81
2	14	2	35.99	34.25
3	14	2	31.62	31.10
4	14	2	16.09	11.84
5	14	2	54.64	54.25
6	14	2	44.50	44.57
7	14	2	21.90	[illegible]
11	14	2	26.64	24.58
13	14	2	27.20	28.14
14	14	2	15.76	20.55
0	15	2	29.67	28.67
1	15	2	23.95	23.73
2	15	2	27.99	27.89

Table 2 (cont.)

with that supposed by the chemical and spectrographic investigations. The latter structure is then formulated as 2α,3β-dihydroxy fern-9(11)-en-23-oic acid which is found to be one of the fernane group triterpenes having all *trans* ring junctures between A and B, C and D, D

and E. This is the first example of the migrated hopane found in lichens.

The bond lengths and angles, calculated from the co-ordinates given in Table 1, are shown in Figs. 3 and 4, respectively. These values are not significantly different

from the expected ones. The mean estimated standard deviations in bond distances are 0·022 Å for C–Br, 0·026 Å for C–C and 0·024 Å for C–O bonds. Those in bond angles are 1·5° for tetrahedral C–C–C and 1·9° for aromatic C–C–C bonds. The mean values of the C–C single bond lengths for the various types of bonds are calculated to be 1·54 Å.

Table 3. *Comparison of the observed and calculated intensity differences used for the establishment of the absolute configuration*

h	k	l	$F_c^2(hkl)/F_c^2(h\bar{k}l)$	$I_o^2(hkl)/I_o^2(h\bar{k}l)$
8	1	1	0.772	>1
2	2	1	0·843	>1
10	2	1	0·632	>1
9	3	1	1·549	<1
5	4	1	1·530	<1
7	4	1	0·267	>1
11	4	1	0·792	>1
13	4	1	1·183	<1
7	5	1	0·829	>1
12	6	1	1·540	<1
13	6	1	0·750	>1

The deviations of atoms from the best planes through the various groups of atoms and the torsion angles in the rings are shown in Tables 4 and 5. Each of the A and D rings takes a slightly deformed chair conformation while the B ring takes a deformed boat conformation. The C ring adopts a half chair conformation and the five-membered ring E takes an intermediate form between envelope and half-chair conformation. In the latter ring, the displacements of atoms from the plane
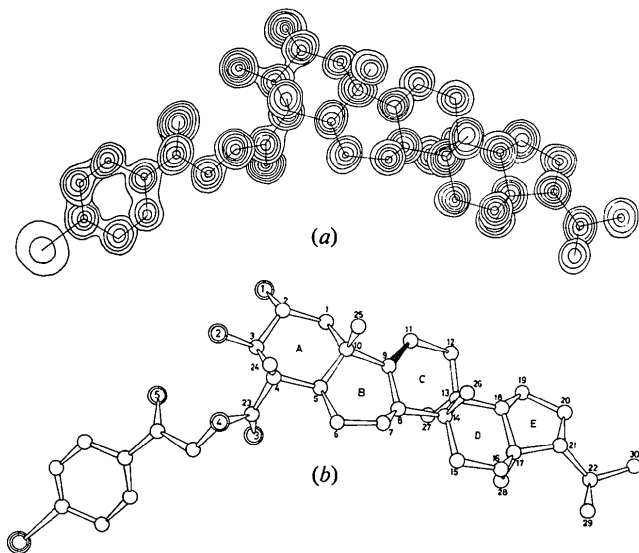

Fig. 2. (a) Composite electron density projection along the a axis. Contours are drawn at intervals of 1 e.Å⁻³ starting at 1·5 e.Å⁻³. Those for the bromine atom are drawn at 2·5 and 25 e.Å⁻³. (b) The molecular structure in the correct absolute configuration. Carbon atoms are shown by a single circle, oxygen by a double circle and bromine by a triple circle. The double bond is shown by a black rod.

formed by C(19), C(20) and C(21) are −0·51 Å and 0·34 Å for C(17) and C(18), respectively. The distortions of the rings seem to be caused mainly by the interactions between the bulky axial groups which push each other in order to relieve the mutual repulsive forces. In a six-membered ring, the non-bonded distances between 1,3 diaxial methyl groups would have been 2·52 Å if the ring took a regular chair form. This distance is here increased to 3·62 Å between C(24) and C(25) and 3·28 Å between C(27) and C(28). In addition to the interaction between C(27) and C(28), repulsions between C(28) and isopropyl side-chain seem to be responsible for the distortion of the five-membered E ring. The isopropyl side-chain extends from C(21) in the α direction. This configuration of C(21) was one of the problems left uncertain by the chemical investigations. As is usually seen in related triterpenes the skeleton of the molecule is slightly bent in a direction opposite to the axial methyl groups at the ring juncture.

Table 4. *Least-squares planes through various groups of atoms and deviations of atoms from the planes*

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 $X \parallel a$, $Y \parallel b$ and $Z \parallel c$.

A ring	$0·869X+0·028Y+0·494Z=3·612$		
C(1)	−0·245	C(10)	0·241
C(2)	0·250	C(23)	−0·692*
C(3)	−0·211	C(24)	1·726*
C(4)	0·189	C(25)	1·736*
C(5)	−0·224		

B ring	$0·815X+0·265Y+0·516Z=5·906$		
C(5)	−0·331	C(9)	0·003
C(6)	−0·046	C(10)	0·367
C(7)	0·377	C(11)	0·072*
C(8)	−0·370	C(25)	1·885*

C ring	$0·774X+0·486Y+0·406Z=8·519$		
C(8)	−0·180	C(13)	−0·336
C(9)	−0·050	C(14)	0·368
C(11)	0·105	C(26)	1·896*
C(12)	0·093	C(27)	−1·873*

D ring	$0·682X+0·507Y+0·528Z=8·538$		
C(13)	−0·249	C(18)	0·250
C(14)	0·247	C(26)	1·784*
C(15)	−0·237	C(27)	−1·776*
C(16)	0·208	C(28)	−1·676*
C(17)	−0·219		

E ring	$0·689X+0·231Y+0·687Z=3·870$		
C(19)	0·0	C(17)	−0·507*
C(20)	0·0	C(18)	0·341*
C(21)	0·0		

Double bond	$0·824X+0·474Y+0·310Z=8·440$		
C(8)	0·005	C(11)	0·020
C(9)	−0·005	C(12)	−0·013
C(10)	−0·007		

* These atoms are not included in the least-squares calculation. Interplanar angles: A/B 166°, B/C 166°, C/D 171°, D/E 165°.
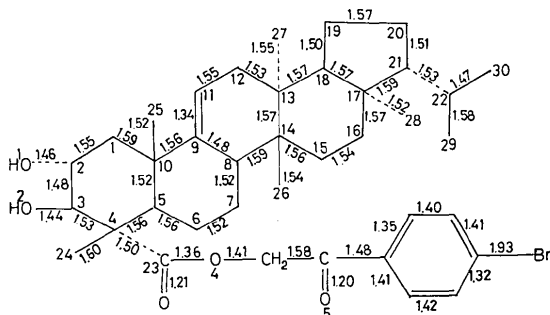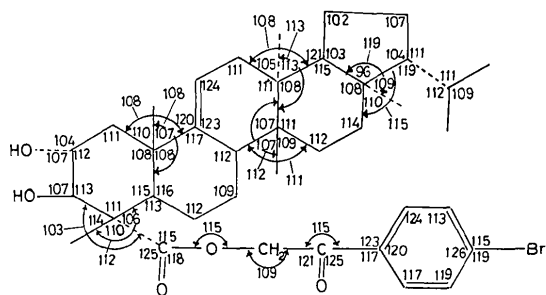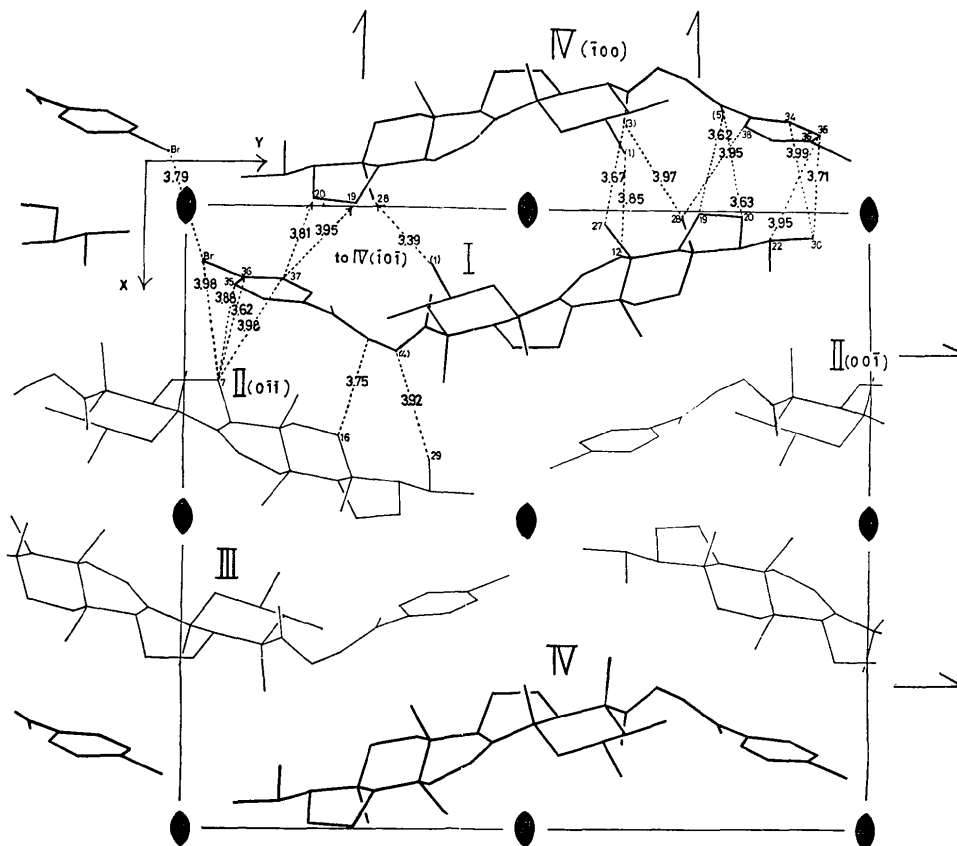
Fig. 3. Bond lengths (Å).

Fig. 4. Bond angles (°).

Table 5. *Torsional angles in the rings*

A ring	φ(A–B)	B ring	φ(A–B)
C(1)—C(2)	−57°	C(5)—C(6)	−24°
C(2)—C(3)	56	C(6)—C(7)	−35
C(3)—C(4)	−51	C(7)—C(8)	65
C(4)—C(5)	52	C(8)—C(9)	−33
C(5)—C(10)	−53	C(9)—C(10)	−25
C(10)-C(1)	55	C(10)-C(5)	55

C ring		D ring	
C(8)—C(9)	19	C(13)-C(14)	−56
C(9)—C(11)	3	C(14)-C(15)	56
C(11)-C(12)	9	C(15)-C(16)	−55
C(12)-C(13)	−43	C(16)-C(17)	52
C(13)-C(14)	66	C(17)-C(18)	−55
C(8)—C(14)	−51	C(13)-C(18)	58

E ring	
C(17)-C(18)	52
C(18)-C(19)	−41
C(19)-C(20)	13
C(20)-C(21)	19
C(17)-C(21)	−40

φ(A–B), a simplified notation of φ(C–A–B–D), is the torsional angle about the A–B bond, in which atoms A, B, C and D are all involved in the ring in question. φ(C–A–B–D) is defined as the angle between the projections of C–A and B–D bonds, when the projection is taken along the A–B bond. The positive angle is taken in the same sense as that of the turning direction of a right handed screw advancing along the A–B bond.

Fig. 5. Projection of the crystal structure along the c axis. Intermolecular short distances less than 4 Å are shown by dotted lines.
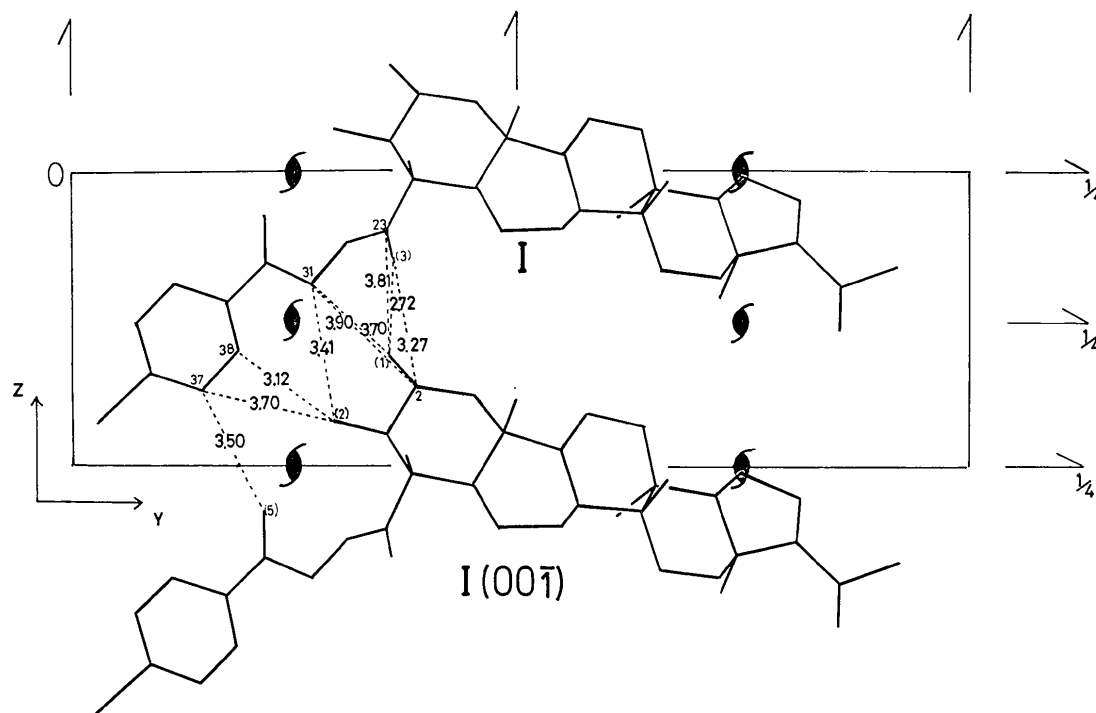
Fig. 6. Projection of the crystal structure along the *a* axis. Intermolecular short distances less than 4 Å between the molecules translated in c are shown by dotted lines.

The crystal structure

The projections of the crystal structure viewed along the *c* and *a* axis are shown in Figs. 5 and 6, respectively. The short intermolecular distances less than 4 Å, from molecule I to the surrounding molecules, are also shown in these Figures. The positions of the molecules are:

I   at x, y, z,
II   at $\frac{1}{2}-x, \frac{1}{2}+y, -z$,
III at $\frac{1}{2}+x, \frac{1}{2}-y, -z$,
IV   at $1-x, 1-y, z$,

where x, y and z are the coordinates given in Table 1. The molecules are packed together mainly by van der Waals forces and there is no abnormal feature in the packing. Short distances between atoms suggesting hydrogen bonds are:

O(3) I(000)···O(1) I(00$\bar{1}$): 2·72 Å ,
O(1)···O(2)   (intramolecular): 2·80 Å .

The molecules are more closely packed in the c direction through the above mentioned intermolecular hy-drogen bond as well as the van der Waals interactions between the hydroxyl groups of *A* ring and ester groups and benzene ring of the phenacyl group.

References

BERGHUIS, J., HAANAPPEL, IJ. M., POTTERS, M., LOOPSTRA, B. O., MACGILLAVRY, C. H. & VEENENDAAL, A. L. (1955). *Acta Cryst.* **8**, 478.

BIJVOET, J. M., PEERDEMAN, A. F. & VAN BOMMEL, A. J. (1951). *Nature, Lond.* **168**, 271.

DAUBEN, C. H. & TEMPLETON, D. H. (1955). *Acta Cryst.* **18**, 265.

OKAYA, Y. & ASHIDA, T. (1967). *HBLS* IV, *The Universal Crystallographic Computing System* (I), p. 65. The Japa-nese Crystallographic Association.

THOMAS, L. H. & UMEDA, K. (1957). *J. Chem. Phys.* **26**, 293.