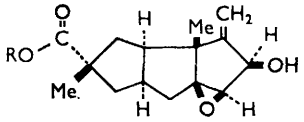
The Structure of Hirsutic Acid. *X*-Ray Analysis of the *p*-Bromophenacyl Ester

By F. W. Comer and J. Trotter

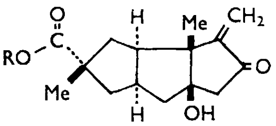
The structure of hirsutic acid has been established by *X*-rays analysis of the *p*-bromophenacyl ester. The crystals are orthorhombic, $a = 6{\cdot}49$, $b = 9{\cdot}14$, $c = 35{\cdot}64$ Å, $Z = 4$, space group $P2_12_12_1$, but irradiation with *X*-rays initiates an unusual molecular rearrangement without disruption of the crystal structure, and with only minor changes in lattice parameters (to $a = 6{\cdot}56$, $b = 9{\cdot}38$, $c = 35{\cdot}14$ Å) and in the intensities of the reflexions. Two complete sets of intensity data were measured with Cu-K_α radiation: the first consisted of 800 reflexions estimated visually from films, and the second of 1379 (984 observed) reflexions measured with a scintillation counter. Structure analysis by Patterson, electron-density, and least-squares methods (final $R = 0{\cdot}136$) indicated that the irradiated crystals contain two different molecules randomly distributed, and established the structure and absolute configuration (anomalous dispersion method) of the *p*-bromophenacyl ester of hirsutic acid, and of the rearrangement product.

The molecules contain three five-membered rings, each of which has an envelope or slightly distorted envelope conformation. The bond distances, and valency angles in both molecules are normal. The most significant intermolecular distances correspond to O–H · · · O hydrogen bonds; these hydrogen bonds are not present in the unirradiated crystals but involve an OH group of the rearrangement product (produced by opening of an epoxide ring of hirsutic acid) and an OH group of the original molecule and/or a carbonyl oxygen of the rearrangement product. All other intermolecular contacts correspond to normal van der Waals interactions.

HIRSUTIC ACID is one of the metabolites isolated from *Stereum hirsutum*.[1] The present Paper describes the determination of its structure by *X*-ray analysis of the *p*-bromophenacyl ester. During the course of the analysis it became apparent that an unusual solid-phase rearrangement was being initiated by the irradiation with *X*-rays, and that an approximately 1 : 1 mixture of the starting material and the rearranged product was being produced, without disrupting the crystal structure, and with only minor changes in lattice parameters and in the intensities of the *X*-ray reflexions. In spite of this complication it was possible, with the help of two pieces of chemical evidence,[2] to determine the structures and absolute configurations of the *p*-bromophenacyl ester of hirsutic acid as (I; R = *p*-bromophenacyl), and hence of hirsutic acid as (I; R = H), and of the rearrangement product as (II; R = *p*-bromophenacyl).



(I)



(II)

EXPERIMENTAL

The *p*-bromophenacyl ester of hirsutic acid was prepared by heating equimolar amounts of hirsutic acid and *p*-bromophenacyl bromide under reflux in dry acetone containing potassium carbonate. Recrystallisation from ethanol gave colourless prisms elongated along *a*, with (001) and (010) developed. The density was measured by flotation in aqueous potassium iodide, and the unit-cell dimensions and space group were determined from various rotation, Weissenberg, and precession photographs, and on the G.E. spectrogoniometer. During the analysis it became apparent that irradiation was initiating a molecular rearrangement, which, however, produced only very minor changes in crystal structure. One manifestation of this rearrangement was a small change in the unit-cell parameters; unit-cell dimensions corresponding as closely as possible to those of the fresh crystals were determined from films with relatively short exposures, and the final cell dimensions were measured on the Spectrogoniometer after the completion of the intensity measurements.

Crystal Data (λ, Cu-K_α = 1·5418 Å; λ, Mo-K_α = 0·7107 Å).—*p*-Bromophenacyl ester of hirsutic acid, $C_{23}H_{25}BrO_5$; *M*, 461·3; m. p. 129—130°. Orthorhombic, initial: $a = 6{\cdot}49 \pm 0{\cdot}03$, $b = 9{\cdot}14 \pm 0{\cdot}03$, $c = 35{\cdot}64 \pm 0{\cdot}08$ Å, Final: $a = 6{\cdot}56 \pm 0{\cdot}03$, $b = 9{\cdot}38 \pm 0{\cdot}03$, $c = 35{\cdot}14 \pm 0{\cdot}08$ Å. $U = 2114$ Å^3 (initial), 2162 Å^3 (final), $D_m = 1{\cdot}46 \pm 0{\cdot}01$ (fresh crystal), $Z = 4$, $D_c = 1{\cdot}45$ (initial), 1·42 (final). Absorption coefficient for *X*-rays, $\mu(\text{Cu-}K_\alpha) = 31$ cm.$^{-1}$ $F(000) = 952$. Space group $P2_12_12_1$ (D_2^4). Absent spectra: $h00$ when h is odd, $0k0$ when k is odd, $00l$ when l is odd.

Three crystals were used to obtain two complete sets of three-dimensional intensity data. The two main crystals had dimensions 1·1, 0·02, and 0·1 mm. parallel to *a*, *b*, and *c*, respectively. One crystal was used to record the intensities on film, and the other for direct intensity measurement by counter techniques. In the film measurements, the intensities of the $0kl$, $1kl$ . . . $4kl$ layers were recorded on equi-inclination Weissenberg films with Cu-K_α radiation, and were estimated visually. The layers were scaled initially by timing the exposures. A third, larger crystal was used for recording the weakest reflexions. A total of 800 reflexions was observed, 150 of these being very weak and visible only on the films of the larger crystal.

For the counter data, the intensities of all reflexions with 2θ (Cu-K_α) $\leqslant 102°$ (corresponding to a minimum interplanar spacing $d = 0{\cdot}99$ Å) were measured on a General Electric XRD-5 Spectrogoniometer, with Single-crystal Orienter, scintillation counter, approximately monochromatic Cu-K_α radiation (nickel filter and pulse-height analyser), and using the moving crystal–moving counter technique.[3] Of the 1379 reflexions in the range $0 < 2\theta$ (Cu-K_α) $\leqslant 102°$, 798 had intensities greater than twice the background, and these were

---

[1] N. G. Heatley, M. A. Jennings, and H. W. Florey, *Brit. J. Exp. Path.*, 1947, **28**, 35.

[2] F. W. Comer, F. McCapra, I. H. Qurreshi, A. I. Scott, and J. Trotter, *Chem. Comm.*, 1965, 310.

[3] T. C. Furnas, " Single Crystal Orienter Instruction Manual," General Electric Company, Milwaukee, 1957.

TABLE 1

Measured and calculated structure amplitudes

h	k	l	F_o	F_c
0	0	2	33.8	52.9
0	0	4	22.6	22.5
0	0	6	83.9	95.0
0	0	8	10.0	26.6
0	0	10	108.4	121.4
0	0	12	68.2	66.5
0	0	14	61.8	71.1
0	0	16	25.6	24.8
0	0	18	49.7	54.8
0	0	20	32.4	35.2
0	0	22	6.0	3.9
0	0	24	26.6	28.4
0	0	26	6.7	4.2
0	0	28	20.8	22.9
0	0	30	6.3	2.2
0	0	32	0.	0.1
0	0	34	8.2	6.2
0	2	0	231.7	240.4
0	2	2	123.7	126.3
0	2	4	104.8	109.6
0	2	6	66.0	68.7
0	2	8	18.2	26.4
0	2	10	132.6	138.8
0	2	12	15.8	16.6
0	2	14	12.5	22.2
0	2	16	35.0	41.5
0	2	18	48.4	54.1
0	2	20	21.8	28.2
0	2	22	9.2	9.1
0	2	24	12.2	18.3
0	2	26	17.1	15.2
0	2	28	12.3	11.0
0	2	30	8.9	7.8
0	2	32	0.	8.5
0	2	34	0.	6.3
0	4	0	60.8	57.0
0	4	2	48.1	47.8
0	4	4	21.1	23.3
0	4	6	36.7	35.9
0	4	8	30.1	25.0
0	4	10	58.2	58.2
0	4	12	35.1	31.4
0	4	14	40.4	44.9
0	4	16	9.5	11.6
0	4	18	12.1	15.0
0	4	20	10.8	9.4
0	4	22	0.	2.3
0	4	24	11.7	14.7
0	4	26	12.0	14.3
0	4	28	9.7	5.8
0	4	30	0.	3.1
0	4	32	0.	4.9
0	6	0	0.	4.8
0	6	2	5.3	7.8
0	6	4	10.7	6.7
0	6	6	7.0	5.8
0	6	8	14.3	13.5
0	6	10	8.0	6.5
0	6	12	4.7	3.4
0	6	14	9.1	6.6
0	6	16	21.4	19.4
0	6	18	6.2	3.0
0	6	20	0.	0.1
0	6	22	0.	3.1
0	6	24	0.	0.7
0	6	26	0.	3.5
0	8	0	5.1	0.7
0	8	2	0.	1.4
0	8	4	5.2	1.5
0	8	6	0.	3.1
0	8	8	0.	0.9
0	8	10	0.	0.1
0	8	12	0.	3.9
0	8	14	0.	3.0
0	8	16	0.	2.8
0	8	18	0.	3.3
1	1	1	54.9	48.0
1	1	3	91.1	89.7
1	1	5	144.8	139.3
1	1	7	41.9	39.6
1	1	9	51.8	49.9
1	1	11	23.8	17.8
1	1	13	23.5	29.5
1	1	15	32.2	32.7
1	1	17	8.9	2.5
1	1	19	29.7	34.1
1	1	21	18.7	16.9
1	1	23	18.6	21.3
1	1	25	8.1	7.3
1	1	27	13.4	16.2
1	1	29	10.1	11.7
1	1	31	0.	1.0
1	1	33	0.	0.5
1	3	1	16.0	12.5
1	3	3	52.9	49.4
1	3	5	37.8	42.1
1	3	7	81.0	78.9
1	3	9	23.8	24.9
1	3	11	23.5	23.8
1	3	13	35.3	38.0
1	3	15	10.6	15.5
1	3	17	25.8	26.9
1	3	19	11.4	16.4
1	3	21	11.6	16.2
1	3	23	13.5	14.9
1	3	25	9.3	12.7
1	3	27	0.	5.3
1	3	29	10.9	15.2
1	3	31	5.1	7.3
1	3	33	0.	3.2
1	5	1	30.7	28.8
1	5	3	53.3	51.1
1	5	5	11.6	13.9
1	5	7	27.5	25.4
1	5	9	13.2	12.5
1	5	11	18.3	19.4
1	5	13	18.6	18.9
1	5	15	10.3	8.9
1	5	17	15.8	14.6
1	5	19	13.0	13.9
1	5	21	10.7	13.3
1	5	23	10.3	9.0
1	5	25	8.2	9.1
1	5	27	6.3	5.2
1	5	29	0.	4.9
1	7	1	6.9	7.9
1	7	3	20.7	17.0
1	7	5	10.5	8.7
1	7	7	23.1	21.6
1	7	9	6.2	7.2
1	7	11	7.2	9.1
1	7	13	0.	4.8
1	7	15	3.7	6.3
1	7	17	7.4	11.2
1	7	19	0.	3.5
1	7	21	8.2	7.5
1	9	1	0.	1.3
1	9	3	0.	2.6
1	9	5	5.1	4.8
1	9	7	0.	9.4
2	0	0	0.	6.9
2	0	2	21.5	31.8
2	0	4	24.5	18.8
2	0	6	21.7	27.1
2	0	8	9.0	1.8
2	0	10	20.5	17.7
2	0	12	27.2	29.5
2	0	14	19.7	16.9
2	0	16	3.8	7.7
2	0	18	7.1	18.1
2	0	20	0.	3.7
2	0	22	0.	0.7
2	0	24	7.6	6.6
2	0	26	13.2	14.3
2	0	28	0.	0.8
2	0	30	7.4	9.9
2	0	32	0.	5.8
2	2	0	27.6	26.9
2	2	2	30.1	27.8
2	2	4	10.9	6.8
2	2	6	51.3	47.3
2	2	8	22.4	22.0
2	2	10	24.9	27.4
2	2	12	29.1	28.4
2	2	14	0.	2.9
2	2	16	17.0	17.7
2	2	18	9.0	11.0
2	2	20	8.3	12.9
2	2	22	0.	8.1
2	2	24	0.	7.7
2	2	26	6.2	11.1
2	2	28	0.	4.9
2	2	30	0.	1.0
2	2	32	0.	1.6
2	4	0	9.9	1.5
2	4	2	42.7	41.3
2	4	4	24.8	24.4
2	4	6	45.3	40.0
2	4	8	25.2	22.6
2	4	10	18.4	16.2
2	4	12	30.1	28.6
2	4	14	20.9	20.9
2	4	16	15.2	19.7
2	4	18	16.3	14.9
2	4	20	10.4	12.1
2	4	22	14.2	16.6
2	4	24	5.1	8.4
2	4	26	8.2	12.1
2	4	28	0.	0.5
2	4	30	0.	2.5
2	6	0	0.	5.7
2	6	2	21.3	15.6
2	6	4	18.8	17.0
2	6	6	18.7	16.8
2	6	8	17.7	15.9
2	6	10	11.5	10.5
2	6	12	25.4	24.6
2	6	14	15.2	10.5
2	6	16	0.	6.2
2	6	18	9.7	7.4
2	6	20	5.2	6.4
2	6	22	9.8	10.2
2	6	24	0.	1.4
2	8	0	0.	1.2
2	8	2	7.4	5.5
2	8	4	6.4	7.5
2	8	6	0.	4.3
2	8	8	0.	5.8
2	8	10	0.	7.5
2	8	12	14.2	13.2
2	8	14	0.	3.7
3	1	1	37.0	28.3
3	1	3	39.5	37.4
3	1	5	62.6	53.0
3	1	7	26.3	21.7
3	1	9	23.1	20.4
3	1	11	35.8	37.4
3	1	13	24.3	24.9
3	1	15	29.2	33.8
3	1	17	0.	4.5
3	1	19	15.6	18.1
3	1	21	13.1	13.8
3	1	23	12.7	14.4
3	1	25	13.0	14.4
3	1	27	0.	3.1
3	1	29	8.1	9.7
3	1	31	0.	4.1
3	3	1	35.5	28.6
3	3	3	40.5	38.7
3	3	5	34.9	31.1
3	3	7	28.9	25.8
3	3	9	30.8	25.2
3	3	11	19.3	14.5
3	3	13	7.0	8.5
3	3	15	27.3	24.9
3	3	17	16.8	19.6
3	3	19	15.5	13.2
3	3	21	10.7	11.8
3	3	23	0.	6.4
3	3	25	0.	5.1
3	3	27	0.	3.0
3	3	29	0.	5.8
3	5	1	18.4	14.4
3	5	3	15.4	14.5
3	5	5	15.6	11.8
3	5	7	13.0	11.8
3	5	9	16.7	11.5
3	5	11	6.0	11.2
3	5	13	10.6	12.4
3	5	15	12.5	9.1
3	5	17	20.7	18.8
3	5	19	24.2	21.4
3	5	21	6.4	5.1
3	5	23	0.	2.9
3	5	25	0.	2.6
3	7	1	5.2	3.7
3	7	3	5.2	6.2
3	7	5	5.2	5.0
3	7	7	0.	12.6
3	7	9	6.4	6.8
3	7	11	0.	5.9
3	7	13	0.	7.6
3	7	15	0.	3.3
3	7	17	0.	7.7
4	0	0	42.6	36.4
4	0	2	7.8	10.9
4	0	4	29.6	25.9
4	0	6	11.3	3.9
4	0	8	24.3	20.5
4	0	10	16.1	17.9
4	0	12	7.3	3.3
4	0	14	31.7	33.7
4	0	16	19.4	23.0
4	0	18	10.6	10.3
4	0	20	12.5	15.4
4	0	22	0.	0.7
4	0	24	0.	5.5
4	0	26	0.	3.5
4	0	28	6.2	4.7
4	2	0	45.0	39.6
4	2	2	13.5	10.8
4	2	4	19.0	17.0
4	2	6	13.8	9.9
4	2	8	22.7	22.1
4	2	10	20.6	20.4
4	2	12	9.4	6.1
4	2	14	21.3	18.0
4	2	16	4.9	12.0
4	2	18	14.6	17.9
4	2	20	10.2	11.0
4	2	22	0.	2.0
4	2	24	9.6	7.6
4	2	26	0.	7.1
4	4	0	22.2	21.9
4	4	2	9.6	9.9
4	4	4	15.7	14.5
4	4	6	0.	5.0
4	4	8	17.1	16.0
4	4	10	10.0	13.5
4	4	12	0.	5.3
4	4	14	8.9	7.3
4	4	16	0.	4.9
4	4	18	12.2	8.9
4	4	20	0.	1.9
4	4	22	6.3	3.1
4	6	0	0.	3.5
4	6	2	6.4	7.9
4	6	4	0.	4.3
4	6	6	0.	4.3
4	6	8	6.4	7.9
4	6	10	0.	3.4
4	6	12	0.	2.5
4	6	14	0.	3.3
4	6	16	0.	2.7
5	1	1	4.9	6.4
5	1	3	14.0	11.8
5	1	5	6.0	9.2
5	1	7	0.	2.4
5	1	9	5.0	4.1
5	1	11	0.	2.9
5	1	13	0.	2.4
5	1	15	0.	4.9
5	1	17	5.2	3.5
5	1	19	0.	3.1
5	1	21	0.	4.2
5	3	1	7.2	5.2
5	3	3	15.8	11.9
5	3	5	6.3	6.8
5	3	7	5.2	3.4
5	3	9	5.2	5.7
5	3	11	0.	5.0
5	3	13	0.	4.5
5	3	15	0.	1.6
5	3	17	0.	3.7
5	3	19	0.	2.9
5	5	1	0.	4.0
5	5	3	5.2	5.2
5	5	5	0.	4.4
5	5	7	12.2	11.7
5	5	9	0.	2.8
5	5	11	5.2	6.0
5	5	13	6.2	2.5
6	0	0	3.7	10.2
6	0	2	10.4	12.3
6	0	4	5.2	1.6
6	0	6	0.	0.3
6	0	8	0.	5.7
6	0	10	0.	8.0
6	0	12	0.	1.5
6	0	14	0.	7.0
6	2	0	0.	1.4
6	2	2	6.4	4.3
6	2	4	0.	5.0
6	2	6	0.	2.9
6	2	8	0.	0.9
6	2	10	5.1	3.9
6	2	12	0.	1.9
0	2	1	79.0	81.5
0	2	3	17.5	12.5
0	2	5	15.8	22.3
0	2	7	8.2	12.5
0	2	9	17.5	14.2
0	2	11	19.5	20.3
0	2	13	38.8	39.7
0	2	15	29.8	35.8
0	2	17	12.9	18.4
0	2	19	18.4	22.9
0	2	21	16.4	16.6
0	2	23	10.0	11.9
0	2	25	9.4	15.5
0	2	27	0.	0.2
0	2	29	0.	8.7
0	2	31	5.2	7.8
0	2	33	0.	0.3
0	4	1	13.4	9.1
0	4	3	25.5	18.1
0	4	5	46.5	49.6
0	4	7	11.8	17.0
0	4	9	39.5	42.1
0	4	11	26.9	26.1
0	4	13	15.5	14.3
0	4	15	32.2	32.7
0	4	17	16.7	18.4
0	4	19	5.5	8.2
0	4	21	0.	2.1
0	4	23	11.0	15.7
0	4	25	6.2	15.0
0	4	27	8.9	9.6
0	4	29	12.7	13.0
0	4	31	0.	1.6
0	6	1	16.4	16.1
0	6	3	31.0	29.4
0	6	5	15.3	12.5
0	6	7	5.5	4.4
0	6	9	28.1	22.1
0	6	11	30.3	30.9
0	6	13	0.	5.0
0	6	15	16.7	16.1
0	6	17	0.	6.4
0	6	19	8.9	12.8
0	6	21	0.	0.9
0	6	23	0.	4.3
0	6	25	11.5	14.6
0	6	27	0.	0.9
0	8	1	25.5	23.4
0	8	3	0.	2.6
0	8	5	0.	3.0
0	8	7	0.	1.4
0	8	9	0.	7.6
0	8	11	6.4	7.3
0	8	13	0.	2.8
0	8	15	5.2	7.6
0	8	17	0.	1.1
1	1	0	118.8	112.3
1	1	2	64.3	60.7
1	1	4	44.9	44.0
1	1	6	86.4	92.4
1	1	8	115.7	115.4
1	1	10	48.3	51.6
1	1	12	36.0	43.4
1	1	14	28.3	23.4
1	1	16	42.7	50.4
1	1	18	39.5	44.5
1	1	20	10.3	9.9
1	1	22	9.2	13.2
1	1	24	10.2	10.1
1	1	26	14.4	18.8
1	1	28	8.7	9.5
1	1	30	0.	2.9
1	1	32	7.3	6.0
1	1	34	0.	4.5
1	3	0	35.6	37.9
1	3	2	37.5	40.3
1	3	4	46.1	46.2
1	3	6	31.2	27.4
1	3	8	17.7	24.5
1	3	10	55.0	51.7
1	3	12	26.3	26.8
1	3	14	19.5	20.5
1	3	16	17.0	21.9
1	3	18	31.1	30.8
1	3	20	11.7	13.7
1	3	22	15.8	21.8
1	3	24	0.	5.6
1	3	26	10.6	13.9
1	3	28	0.	5.4
1	3	30	0.	7.7
1	3	32	0.	6.0
1	5	0	36.9	43.3
1	5	2	11.7	14.2
1	5	4	27.4	23.7
1	5	6	38.2	38.6
1	5	8	13.7	13.5
1	5	10	25.6	21.9
1	5	12	0.	7.1
1	5	14	17.6	16.9
1	5	16	5.7	8.5
1	5	18	0.	2.4
1	5	20	10.0	11.9
1	5	22	14.8	12.4
1	5	24	0.	5.7
1	5	26	6.4	7.6
1	5	28	5.1	5.5
1	7	0	12.9	12.9
1	7	2	0.	0.5
1	7	4	16.7	16.6
1	7	6	18.6	16.9
1	7	8	0.	4.3
1	7	10	0.	4.1
1	7	12	0.	7.9
1	7	14	0.	2.1
1	7	16	13.3	13.8
1	7	18	5.2	3.9
1	7	20	0.	7.9
1	7	22	0.	1.0
1	9	0	0.	2.1
1	9	2	0.	1.0
1	9	4	7.3	7.3
1	9	6	0.	4.9
1	9	8	0.	2.5
2	0	1	25.6	26.2
2	0	3	137.2	125.5
2	0	5	25.4	20.1
2	0	7	80.8	75.2
2	0	9	21.6	24.3
2	0	11	86.9	86.9
2	0	13	83.8	85.5
2	0	15	25.4	21.3
2	0	17	19.0	25.5
2	0	19	11.1	11.5
2	0	21	22.2	24.2
2	0	23	23.4	26.3
2	0	25	6.0	6.0
2	0	27	0.	3.4
2	0	29	0.	0.4
2	0	31	0.	8.0
2	0	33	0.	4.0
2	2	1	42.1	34.4
2	2	3	91.0	83.9
2	2	5	16.3	21.9
2	2	7	47.1	48.0
2	2	9	20.3	17.3
2	2	11	57.5	60.8
2	2	13	50.0	57.3
2	2	15	6.2	3.3
2	2	17	33.3	35.0
2	2	19	6.9	5.7
2	2	21	12.1	27.3
2	2	23	21.9	24.8
2	2	25	7.0	10.9
2	2	27	5.1	7.8
2	2	29	0.	2.4
2	2	31	5.1	7.6
2	4	1	23.7	20.7
2	4	3	36.4	39.4
2	4	5	18.6	16.3
2	4	7	12.1	13.3
2	4	9	0.	6.3
2	4	11	22.9	19.1
2	4	13	22.7	25.2
2	4	15	22.3	25.0
2	4	17	13.1	14.9
2	4	19	4.8	11.1
2	4	21	12.6	18.7
2	4	23	11.4	13.2
2	4	25	0.	4.3
2	4	27	6.3	5.5
2	4	29	0.	2.3
2	6	1	5.7	4.2
2	6	3	13.6	13.3
2	6	5	17.0	14.2
2	6	7	0.	7.3
2	6	9	6.9	9.1
2	6	11	0.	4.0
2	6	13	19.5	19.0
2	6	15	17.7	15.8
2	6	17	0.	2.7
2	6	19	0.	2.1
2	6	21	0.	3.1
2	6	23	0.	3.2
2	8	1	0.	2.8
2	8	3	3.7	2.7
2	8	5	5.2	7.1
2	8	7	0.	1.2
2	8	9	0.	8.7
2	8	11	0.	4.0
2	8	13	0.	1.5
2	8	15	0.	4.0
3	1	0	0.	5.0
3	1	2	19.1	20.1
3	1	4	21.7	25.2
3	1	6	37.8	39.1
3	1	8	36.7	41.8
3	1	10	14.8	23.0
3	1	12	8.4	12.2
3	1	14	6.5	5.9
3	1	16	0.	4.4
3	1	18	8.5	11.0
3	1	20	7.4	8.5
3	1	22	0.	4.0
3	1	24	5.0	1.2
3	1	26	0.	3.0
3	1	28	0.	3.7
3	1	30	0.	4.0
3	3	0	45.9	44.1
3	3	2	17.4	14.5
3	3	4	17.5	14.7
3	3	6	9.0	12.9
3	3	8	8.3	10.6
3	3	10	32.3	31.4
3	3	12	6.9	5.2
3	3	14	11.9	12.9
3	3	16	10.9	15.4
3	3	18	21.8	27.1
3	3	20	15.7	19.8
3	3	22	0.	2.8
3	3	24	7.3	7.6
3	3	26	6.3	7.7
3	3	28	0.	6.1
3	5	0	31.9	28.2
3	5	2	17.3	12.6
3	5	4	20.9	18.9
3	5	6	14.2	13.7
3	5	8	16.9	16.3
3	5	10	20.4	17.4
3	5	12	0.	2.8
3	5	14	13.8	15.5
3	5	16	7.3	10.1
3	5	18	18.8	18.9
3	5	20	15.7	12.9
3	5	22	0.	0.4
3	5	24	0.	2.5
3	7	0	13.2	13.8
3	7	2	0.	2.5
3	7	4	14.8	14.1
3	7	6	0.	5.1
3	7	8	0.	4.1
3	7	10	11.7	10.6
3	7	12	0.	3.3
3	7	14	15.6	12.5
3	7	16	0.	1.2
4	0	1	0.	1.1
4	0	3	15.1	10.8
4	0	5	4.2	6.7
4	0	7	22.8	17.3
4	0	9	0.	7.5
4	0	11	0.	7.5
4	0	13	0.	9.1
4	0	15	0.	4.4
4	0	17	16.7	18.8
4	0	19	6.2	3.0
4	0	21	14.6	16.8
4	0	23	0.	0.8
4	0	25	0.	10.2
4	0	27	5.1	6.0
4	2	1	18.4	14.4
4	2	3	15.2	10.6
4	2	5	12.9	8.2
4	2	7	14.6	11.9
4	2	9	17.6	12.4
4	2	11	17.1	18.2
4	2	13	11.7	12.8
4	2	15	12.9	15.7
4	2	17	7.9	4.5
4	2	19	0.	3.9
4	2	21	0.	5.7
4	2	23	8.2	3.2
4	2	25	10.9	8.2
4	2	27	5.0	5.5
4	4	1	20.1	13.3
4	4	3	21.6	15.3
4	4	5	13.3	7.8
4	4	7	24.1	18.8
4	4	9	17.3	16.1
4	4	11	16.4	15.2
4	4	13	0.	7.1
4	4	15	10.4	7.0
4	4	17	9.7	6.2
4	4	19	0.	5.1
4	4	21	0.	4.6
4	4	23	8.0	7.8
4	6	1	18.0	13.4
4	6	3	6.4	3.0
4	6	5	12.3	7.4
4	6	7	0.	2.1
4	6	9	9.8	7.0
4	6	11	6.4	7.5
4	6	13	0.	2.5
4	6	15	0.	4.5
5	1	0	0.	5.2
5	1	2	37.2	27.9
5	1	4	27.1	22.3
5	1	6	11.6	7.2
5	1	8	27.8	20.8
5	1	10	0.	2.5
5	1	12	15.6	9.5
5	1	14	8.9	5.8
5	1	16	8.1	5.4
5	1	18	8.9	8.0
5	1	20	0.	7.2
5	1	22	10.1	10.0
5	3	0	0.	3.7
5	3	2	22.9	13.9
5	3	4	17.0	11.2
5	3	6	23.0	20.8
5	3	8	26.2	20.3
5	3	10	0.	5.0
5	3	12	16.5	11.7
5	3	14	5.2	2.9
5	3	16	0.	5.0
5	3	18	0.	2.7
5	5	0	0.	2.6
5	5	2	11.6	6.9
5	5	4	5.2	3.1
5	5	6	9.0	9.7
5	5	8	9.0	7.6
5	5	10	0.	3.4
5	5	12	0.	5.6
6	0	1	7.4	8.6
6	0	3	11.7	9.7
6	0	5	0.	7.0
6	0	7	0.	4.7
6	0	9	0.	0.0
6	0	11	0.	2.4
6	0	13	0.	4.8
6	2	1	5.2	5.1
6	2	3	12.2	12.9
6	2	5	7.4	7.0
6	2	7	0.	4.3
6	2	9	0.	4.7
6	2	11	8.0	6.0
0	1	3	23.6	33.7
0	1	5	49.0	48.8
0	1	7	22.7	26.7
0	1	9	29.5	32.8
0	1	11	51.1	59.6
0	1	13	27.8	30.8
0	1	15	35.4	42.6
0	1	17	26.9	37.1
0	1	19	0.	3.1
0	1	21	16.1	27.3
0	1	23	8.2	15.0
0	1	25	18.8	23.4
0	1	27	15.4	24.8

TABLE 1 (*Continued*)

h	*k*	*l*	F_o	F_c
0	3	29	0.	0.2
0	3	31	10.3	19.0
0	3	33	0.	7.1
0	3	35	9.4	12.9
0	3	1	83.6	78.6
0	3	3	60.5	58.7
0	3	5	7.0	14.5
0	3	7	32.3	38.9
0	3	9	7.1	0.8
0	3	11	13.2	3.0
0	3	13	7.9	6.9
0	3	15	17.4	17.2
0	3	17	18.9	25.8
0	3	19	5.2	2.4
0	3	21	19.2	25.1
0	3	23	4.7	2.6
0	3	25	15.9	19.2
0	3	27	10.7	14.3
0	3	29	0.	1.1
0	3	31	0.	0.9
0	3	33	0.	2.7
0	5	1	2.7	5.1
0	5	3	35.5	35.0
0	5	5	4.8	8.4
0	5	7	13.2	14.9
0	5	9	4.1	5.0
0	5	11	0.	6.1
0	5	13	0.	2.3
0	5	15	9.1	1.3
0	5	17	0.	2.2
0	5	19	10.9	8.5
0	5	21	7.9	12.4
0	5	23	0.	4.7
0	5	25	5.2	4.7
0	5	27	0.	2.0
0	5	29	0.	3.7
0	7	1	4.8	3.5
0	7	3	15.3	15.8
0	7	5	4.9	5.7
0	7	7	0.	2.9
0	7	9	12.2	12.5
0	7	11	0.	4.0
0	7	13	7.2	7.9
0	7	15	0.	5.7
0	7	17	5.2	0.9
0	7	19	0.	0.7
0	7	21	0.	3.2
0	7	23	0.	2.9
0	9	1	0.	4.8
0	9	3	10.3	10.0
0	9	5	6.3	4.3
0	9	7	0.	5.5
0	9	9	5.1	2.4
1	0	2	39.2	34.8
1	0	4	161.5	164.9
1	0	6	42.5	41.5
1	0	8	33.7	41.7
1	0	10	13.6	9.0
1	0	12	52.3	57.0
1	0	14	21.3	22.3
1	0	16	20.8	20.4
1	0	18	21.1	27.2
1	0	20	0.	1.1
1	0	22	19.3	24.7
1	0	24	0.	2.5
1	0	26	0.	9.4
1	0	28	16.3	22.1
1	0	30	11.6	11.3
1	0	32	12.2	19.3
1	0	34	0.	5.9
1	2	0	26.9	27.3
1	2	2	44.1	47.7
1	2	4	86.8	77.2
1	2	6	89.0	86.8
1	2	8	88.1	85.2
1	2	10	13.9	14.2
1	2	12	28.5	27.1
1	2	14	26.8	26.9
1	2	16	8.3	7.7
1	2	18	18.9	21.4
1	2	20	7.3	9.0
1	2	22	19.8	23.8
1	2	24	0.	11.8
1	2	26	12.9	14.1
1	2	28	6.2	6.5
1	2	30	0.	6.2
1	2	32	0.	9.8
1	2	34	0.	5.3
1	4	0	46.8	51.0
1	4	2	32.6	35.1
1	4	4	29.9	32.0
1	4	6	69.9	67.2
1	4	8	35.6	38.6
1	4	10	13.9	19.3
1	4	12	6.3	6.0
1	4	14	32.0	32.6
1	4	16	6.8	5.5
1	4	18	8.4	12.8
1	4	20	9.4	9.1
1	4	22	6.9	12.2
1	4	24	8.7	7.0
1	4	26	0.	3.8
1	4	28	0.	6.1
1	4	30	0.	4.9
1	6	0	24.1	23.6
1	6	2	8.8	9.6
1	6	4	24.0	21.8
1	6	6	11.5	8.5
1	6	8	10.3	12.9
1	6	10	23.0	23.7
1	6	12	0.	6.9
1	6	14	19.3	16.0
1	6	16	12.8	13.5
1	6	18	8.9	9.2
1	6	20	8.2	10.8
1	6	22	0.	2.5
1	6	24	0.	1.2
1	6	26	0.	1.4
1	8	0	16.4	14.5
1	8	2	0.	6.2
1	8	4	7.3	7.3
1	8	6	7.4	7.7
1	8	8	9.8	9.6
1	8	10	0.	7.4
1	8	12	0.	4.7
1	8	14	0.	6.6
1	8	16	0.	5.2
2	1	1	46.0	43.9
2	1	3	31.9	31.4
2	1	5	14.3	10.7
2	1	7	67.5	70.1
2	1	9	34.3	33.2
2	1	11	38.2	43.1
2	1	13	28.8	29.0
2	1	15	25.1	23.5
2	1	17	24.3	19.8
2	1	19	8.9	6.9
2	1	21	8.3	7.8
2	1	23	4.7	8.7
2	1	25	6.0	7.6
2	1	27	5.0	6.3
2	1	29	0.	8.6
2	1	31	0.	2.5
2	1	33	0.	1.5
2	3	1	37.5	29.6
2	3	3	20.0	22.3
2	3	5	29.5	24.5
2	3	7	22.7	16.3
2	3	9	48.6	48.0
2	3	11	61.8	61.4
2	3	13	6.9	9.7
2	3	15	21.0	21.6
2	3	17	6.9	11.7
2	3	19	17.9	15.7
2	3	21	11.2	6.5
2	3	23	4.9	3.4
2	3	25	13.0	16.4
2	3	27	8.1	6.8
2	3	29	5.2	5.7
2	3	31	0.	3.8
2	5	1	41.2	38.8
2	5	3	0.	12.8
2	5	5	22.6	21.9
2	5	7	0.	0.3
2	5	9	33.5	34.8
2	5	11	22.6	21.3
2	5	13	18.5	15.9
2	5	15	26.7	31.5
2	5	17	9.3	5.7
2	5	19	14.8	10.3
2	5	21	6.3	6.7
2	5	23	9.0	6.1
2	5	25	8.2	7.7
2	5	27	0.	2.5
2	7	1	18.5	17.7
2	7	3	15.9	15.5
2	7	5	5.1	13.0
2	7	7	5.1	5.3
2	7	9	12.1	11.7
2	7	11	7.3	12.1
2	7	13	11.7	7.6
2	7	15	13.9	14.7
2	7	17	0.	3.7
2	7	19	5.2	6.5
3	0	2	79.2	68.8
3	0	4	21.9	19.7
3	0	6	40.8	41.5
3	0	8	55.2	54.5
3	0	10	0.	16.2
3	0	12	61.0	57.6
3	0	14	12.7	6.7
3	0	16	16.8	17.6
3	0	18	13.2	13.4
3	0	20	9.4	10.9
3	0	22	17.0	19.9
3	0	24	0.	0.1
3	0	26	11.0	13.5
3	0	28	0.	4.0
3	0	30	0.	3.5
3	2	0	9.6	6.8
3	2	2	35.9	28.8
3	2	4	43.5	40.4
3	2	6	47.5	45.3
3	2	8	52.2	48.1
3	2	10	23.2	27.3
3	2	12	32.2	32.5
3	2	14	9.6	6.5
3	2	16	19.5	20.1
3	2	18	15.0	17.5
3	2	20	7.6	11.7
3	2	22	17.2	19.4
3	2	24	0.	5.3
3	2	26	0.	8.1
3	2	28	0.	2.5
3	2	30	0.	3.8
3	4	0	13.4	15.9
3	4	2	19.0	15.3
3	4	4	11.8	10.9
3	4	6	11.1	11.4
3	4	8	28.3	22.2
3	4	10	12.9	10.9
3	4	12	13.2	14.5
3	4	14	13.1	12.4
3	4	16	13.0	11.3
3	4	18	17.0	15.5
3	4	20	8.1	9.1
3	4	22	8.2	9.2
3	4	24	0.	3.4
3	4	26	8.1	8.1
3	6	0	6.1	4.5
3	6	2	5.0	4.1
3	6	4	3.5	4.0
3	6	6	0.	3.7
3	6	8	6.2	5.3
3	6	10	7.3	5.9
3	6	12	8.2	11.3
3	6	14	7.4	4.6
3	6	16	0.	3.4
3	6	18	11.1	10.9
3	6	20	0.	6.0
3	8	0	0.	2.0
3	8	2	0.	1.2
3	8	4	0.	2.1
3	8	6	0.	2.0
3	8	8	0.	2.8
4	1	1	29.9	23.9
4	1	3	44.6	36.9
4	1	5	15.1	11.3
4	1	7	33.2	26.8
4	1	9	7.6	5.7
4	1	11	18.9	19.3
4	1	13	16.4	18.6
4	1	15	7.5	11.6
4	1	17	19.6	22.5
4	1	19	0.	2.5
4	1	21	10.8	13.1
4	1	23	0.	7.8
4	1	25	0.	1.5
4	1	27	0.	6.4
4	3	1	24.1	25.2
4	3	3	21.5	20.7
4	3	5	4.6	9.2
4	3	7	18.8	15.0
4	3	9	8.3	7.8
4	3	11	18.2	17.4
4	3	13	19.0	19.5
4	3	15	0.	2.4
4	3	17	8.8	8.0
4	3	19	10.3	12.4
4	3	21	6.4	8.5
4	3	23	0.	5.7
4	3	25	0.	2.5
4	5	1	16.7	15.0
4	5	3	7.2	8.2
4	5	5	3.6	5.8
4	5	7	0.	4.2
4	5	9	0.	3.4
4	5	11	13.3	12.9
4	5	13	8.3	8.7
4	5	15	0.	4.4
4	5	17	0.	6.7
4	5	19	0.	3.8
4	7	1	5.2	2.8
4	7	3	0.	2.9
4	7	5	7.3	6.1
4	7	7	0.	3.0
4	7	9	0.	3.0
5	0	2	0.	0.7
5	0	4	0.	6.1
5	0	6	0.	1.3
5	0	8	8.6	12.9
5	0	10	0.	0.9
5	0	12	0.	1.4
5	0	14	0.	0.9
5	0	16	6.4	7.6
5	0	18	0.	3.6
5	0	20	0.	6.2
5	0	22	0.	1.9
5	2	0	5.0	4.6
5	2	2	5.0	4.1
5	2	4	9.4	9.8
5	2	6	7.2	7.2
5	2	8	8.8	11.2
5	2	10	9.5	12.7
5	2	12	0.	8.5
5	2	14	12.7	13.6
5	2	16	0.	1.9
5	2	18	0.	4.5
5	2	20	0.	2.7
5	4	0	14.2	13.9
5	4	2	0.	2.7
5	4	4	15.2	13.3
5	4	6	11.1	10.6
5	4	8	0.	5.8
5	4	10	0.	3.9
5	4	12	0.	3.2
5	4	14	12.7	10.8
5	4	16	0.	3.5
5	6	0	8.8	6.3
5	6	2	0.	3.4
5	6	4	6.2	8.5
6	1	1	13.9	7.7
6	1	3	13.9	7.1
6	1	5	0.	4.5
6	1	7	14.6	12.2
6	1	9	10.3	5.6
6	1	11	7.2	6.2
6	1	13	8.0	4.8
6	3	1	0.	2.7
6	3	3	7.3	2.7
6	3	5	5.2	4.1
6	3	7	10.9	7.7
0	1	2	44.7	47.2
0	1	4	87.6	91.8
0	1	6	77.9	77.7
0	1	8	5.0	11.4
0	1	10	13.0	23.1
0	1	12	28.6	33.8
0	1	14	40.5	41.6
0	1	16	9.9	13.2
0	1	18	11.6	17.5
0	1	20	3.9	4.8
0	1	22	9.4	15.1
0	1	24	4.5	0.2
0	1	26	11.1	7.7
0	1	28	12.6	5.0
0	1	30	10.8	8.8
0	1	32	0.	4.7
0	1	34	0.	2.5
0	3	2	66.1	68.9
0	3	4	9.6	8.9
0	3	6	52.8	55.1
0	3	8	26.9	29.5
0	3	10	20.5	17.7
0	3	12	57.0	62.0
0	3	14	54.6	54.7
0	3	16	8.6	14.3
0	3	18	11.6	16.0
0	3	20	0.	4.5
0	3	22	28.2	30.5
0	3	24	0.	4.0
0	3	26	9.9	14.0
0	3	28	0.	0.8
0	3	30	0.	5.1
0	3	32	6.3	5.5
0	5	2	44.0	47.9
0	5	4	44.1	41.0
0	5	6	53.6	54.3
0	5	8	36.0	36.1
0	5	10	22.7	23.8
0	5	12	22.5	24.3
0	5	14	13.0	10.4
0	5	16	19.9	20.7
0	5	18	19.4	17.3
0	5	20	17.5	22.1
0	5	22	19.5	21.8
0	5	24	6.3	7.4
0	5	26	9.7	12.6
0	5	28	0.	9.2
0	7	2	30.0	29.6
0	7	4	16.8	17.6
0	7	6	16.3	13.2
0	7	8	24.5	26.5
0	7	10	5.0	3.7
0	7	12	24.2	23.7
0	7	14	5.2	6.7
0	7	16	19.5	14.2
0	7	18	0.	3.6
0	7	20	0.	8.2
0	7	22	11.6	10.4
0	9	2	9.0	9.2
0	9	4	7.3	9.1
0	9	6	0.	2.2
0	9	8	7.3	8.0
0	9	10	0.	3.0
1	0	1	103.2	108.1
1	0	3	65.7	72.5
1	0	5	72.4	72.2
1	0	7	43.1	46.8
1	0	9	131.2	135.0
1	0	11	4.5	14.9
1	0	13	22.5	14.1
1	0	15	56.3	63.0
1	0	17	0.	3.5
1	0	19	58.2	63.6
1	0	21	23.4	27.9
1	0	23	12.6	18.1
1	0	25	14.1	17.5
1	0	27	0.	1.5
1	0	29	14.4	17.2
1	0	31	0.	5.6
1	0	33	0.	3.7
1	2	1	93.3	89.4
1	2	3	99.3	89.5
1	2	5	57.9	54.1
1	2	7	30.0	28.4
1	2	9	85.3	86.7
1	2	11	78.7	76.3
1	2	13	29.3	30.3
1	2	15	38.4	40.5
1	2	17	8.6	14.3
1	2	19	44.1	44.3
1	2	21	17.0	15.1
1	2	23	7.2	5.0
1	2	25	18.2	22.3
1	2	27	0.	6.1
1	2	29	8.1	9.8
1	2	31	0.	7.3
1	2	33	0.	2.4
1	4	1	51.6	46.8
1	4	3	28.7	25.9
1	4	5	41.0	40.3
1	4	7	28.6	30.6
1	4	9	60.9	59.1
1	4	11	25.7	19.3
1	4	13	10.7	6.1
1	4	15	32.5	32.6
1	4	17	16.1	16.7
1	4	19	13.8	9.3
1	4	21	17.9	21.9
1	4	23	7.0	6.5
1	4	25	9.5	11.7
1	4	27	5.2	3.2
1	4	29	0.	6.3
1	4	31	0.	2.1
1	6	1	6.2	4.4
1	6	3	28.8	27.6
1	6	5	19.0	18.5
1	6	7	27.2	26.1
1	6	9	6.6	9.6
1	6	11	16.1	14.8
1	6	13	5.9	8.0
1	6	15	13.6	18.6
1	6	17	5.1	6.1
1	6	19	6.3	8.5
1	6	21	12.3	12.5
1	6	23	0.	3.6
1	6	25	0.	6.1
1	8	1	0.	2.2
1	8	3	12.7	10.4
1	8	5	8.2	7.1
1	8	7	16.5	14.6
1	8	9	5.2	8.2
1	8	11	6.4	8.7
1	8	13	0.	2.6
1	8	15	0.	7.8
1	8	17	0.	3.3
2	1	0	83.0	81.5
2	1	2	27.0	24.9
2	1	4	107.1	105.2
2	1	6	16.0	12.0
2	1	8	19.4	17.2
2	1	10	45.6	48.1
2	1	12	25.9	27.9
2	1	14	59.3	60.8
2	1	16	29.2	36.3
2	1	18	33.9	37.6
2	1	20	22.0	25.1
2	1	22	6.4	11.5
2	1	24	24.6	27.8
2	1	26	9.3	11.8
2	1	28	11.4	12.7
2	1	30	0.	2.0
2	1	32	6.3	10.0
2	3	0	81.6	85.1
2	3	2	24.4	23.0
2	3	4	40.8	36.7
2	3	6	34.9	29.1
2	3	8	24.2	21.2
2	3	10	50.1	47.3
2	3	12	32.5	34.5
2	3	14	50.6	52.9
2	3	16	19.9	21.9
2	3	18	15.7	16.9
2	3	20	5.7	5.1
2	3	22	10.8	9.9
2	3	24	7.9	6.3
2	3	26	7.2	7.6
2	3	28	8.2	8.1
2	3	30	0.	3.0
2	5	0	33.2	30.5
2	5	2	10.3	9.2
2	5	4	15.6	11.8
2	5	6	0.	5.7
2	5	8	7.0	5.8
2	5	10	25.1	25.3
2	5	12	8.0	6.8
2	5	14	11.7	11.8
2	5	16	9.2	6.9
2	5	18	13.8	10.3
2	5	20	0.	3.8
2	5	22	0.	5.6
2	5	24	0.	4.1
2	5	26	0.	1.9
2	7	0	0.	3.6
2	7	2	6.2	5.4
2	7	4	0.	4.1
2	7	6	0.	3.7
2	7	8	0.	4.6
2	7	10	6.3	5.2
2	7	12	6.4	9.6
2	7	14	0.	6.0
2	7	16	0.	3.9
2	7	18	8.2	6.1
2	7	20	0.	2.2
3	0	1	8.3	4.9
3	0	3	26.0	27.8
3	0	5	24.1	20.1
3	0	7	29.6	29.5
3	0	9	52.0	46.5
3	0	11	16.7	17.7
3	0	13	0.	8.3
3	0	15	22.2	24.2
3	0	17	12.9	17.0
3	0	19	18.2	21.5
3	0	21	4.8	6.7
3	0	23	10.6	9.3
3	0	25	0.	3.0
3	0	27	5.2	8.7
3	0	29	0.	6.7
3	0	31	0.	0.8
3	2	1	3.6	19.8
3	2	3	28.9	24.3
3	2	5	33.1	27.8
3	2	7	30.9	28.5
3	2	9	32.3	32.3
3	2	11	24.5	27.7
3	2	13	14.3	12.4
3	2	15	13.1	10.4
3	2	17	21.6	22.7
3	2	19	10.5	9.9
3	2	21	6.0	10.2
3	2	23	6.2	3.9
3	2	25	0.	3.8
3	2	27	5.2	7.7
3	2	29	0.	4.1
3	4	1	12.0	13.9
3	4	3	24.8	25.2
3	4	5	21.9	26.6
3	4	7	30.4	31.2
3	4	9	11.5	16.1
3	4	11	17.3	17.3
3	4	13	12.5	10.1
3	4	15	6.9	7.6
3	4	17	20.1	21.4
3	4	19	14.7	13.2
3	4	21	9.6	8.2
3	4	23	0.	3.4
3	4	25	0.	3.9
3	4	27	5.1	4.7
3	6	1	13.1	10.6
3	6	3	16.5	10.8
3	6	5	5.0	3.8
3	6	7	17.9	16.1
3	6	9	12.0	7.7
3	6	11	8.9	7.9
3	6	13	0.	7.4
3	6	15	0.	3.0
3	6	17	16.1	12.2
3	6	19	0.	7.0
3	6	21	0.	4.8
3	8	1	0.	4.9
3	8	3	8.9	7.2
3	8	5	0.	3.9
3	8	7	8.9	6.2
3	8	9	0.	2.8
4	1	0	25.9	19.9
4	1	2	28.1	22.5
4	1	4	28.5	25.0
4	1	6	28.2	24.4
4	1	8	14.2	14.7
4	1	10	14.8	14.0
4	1	12	0.	5.2
4	1	14	13.7	17.2
4	1	16	6.8	5.3
4	1	18	0.	1.6
4	1	20	5.1	1.9
4	1	22	5.1	5.5
4	1	24	0.	2.0
4	1	26	0.	5.0
4	3	0	19.8	10.3
4	3	2	29.7	27.0
4	3	4	20.9	16.0
4	3	6	17.4	12.8
4	3	8	18.6	13.3
4	3	10	12.7	11.3
4	3	12	17.4	17.4
4	3	14	5.0	4.6
4	3	16	7.1	4.2
4	3	18	5.1	5.0
4	3	20	7.3	8.7
4	3	22	8.2	8.3
4	3	24	5.1	6.7
4	5	0	0.	1.2
4	5	2	17.8	15.5
4	5	4	13.5	9.7
4	5	6	8.9	10.3
4	5	8	7.3	12.1
4	5	10	14.7	6.2
4	5	12	14.8	15.4
4	5	14	11.1	10.3
4	5	16	0.	0.9
4	5	18	0.	2.6
4	5	20	0.	4.5
4	7	0	7.3	6.9
4	7	2	6.3	5.7
4	7	4	5.2	5.4
4	7	6	0.	5.2
4	7	8	0.	7.8
5	0	1	22.3	19.2
5	0	3	10.9	7.3
5	0	5	16.3	15.6
5	0	7	6.1	4.3
5	0	9	20.1	14.8
5	0	11	13.4	14.1
5	0	13	9.6	8.7
5	0	15	9.0	8.9
5	0	17	0.	5.3
5	0	19	0.	0.2
5	0	21	0.	0.3
5	2	1	12.7	10.7
5	2	3	15.9	12.4
5	2	5	18.9	15.8
5	2	7	0.	4.9
5	2	9	8.0	6.6
5	2	11	0.	6.4
5	2	13	5.2	3.0
5	2	15	8.2	6.8
5	2	17	0.	4.0
5	2	19	8.1	7.3
5	2	21	0.	1.6
5	4	1	5.2	1.4
5	4	3	7.4	7.7
5	4	5	7.4	3.8
5	4	7	5.2	4.5
5	4	9	0.	5.0
5	4	11	0.	5.6
5	4	13	0.	1.5
5	4	15	0.	3.0
5	4	17	0.	2.4
5	6	1	0.	2.1
5	6	3	0.	1.8
6	1	0	23.3	14.7
6	1	2	12.3	8.3
6	1	4	6.4	4.1
6	1	6	5.2	2.2
6	1	8	0.	3.0
6	1	10	7.2	5.1
6	1	12	0.	2.1
6	3	0	7.3	6.1
6	3	2	0.	2.1
6	3	4	5.2	6.0
6	3	6	0.	1.5
6	3	8	0.	4.3

used in the structure determination and refinement. Final structure factors were calculated also for the 186 reflexions with intensity between one and two times the background, and for the 395 unobserved reflexions. For both the visual and counter data, the appropriate Lorentz and polarisation factors were applied, and the structure amplitudes were derived. No absorption corrections were considered necessary. Since the rearrangement was complete after a few hours (see below), both sets of data refer to the fully rearranged structure (approximately 1 : 1) equilibrium being reached during the irradiation in the initial orientation of the crystals.

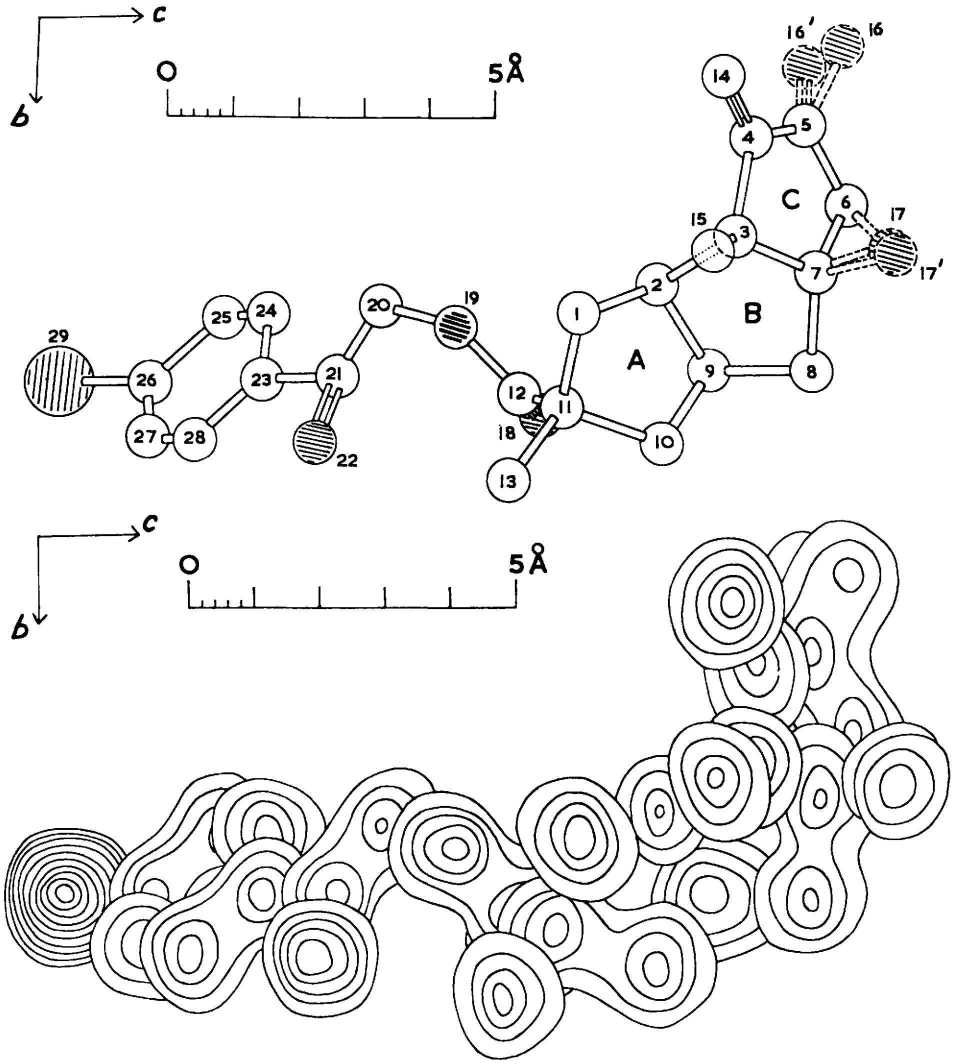


FIGURE 1 Superimposed sections of the three-dimensional electron-density distribution, through the atomic centres parallel to (100); contours for carbon and oxygen atoms are at intervals of 1e. Å^{-3} starting at 1e. Å^{-3}, and for the Br atom at intervals of 3e. Å^{-3} starting at 3e. Å^{-3} A drawing of the molecule is also shown. Both drawings show the correct absolute configuration, the positive direction of the *a*-axis being towards the viewer.

Structure Analysis.—The visual data, obtained first, were used in the preliminary stages of the structure analysis. The position of the bromine atom was determined from the three Harker sections of the three-dimensional Patterson function as (0·101, 0·216, 0·146), and a three-dimensional Fourier series was summed with phases based on the bromine atom. On the resulting electron-density distribution 28 of the 29 non-hydrogen atoms in the molecule were clearly resolved. Structure factors were calculated for the 28 atoms using the scattering factors for Br. C, O of the International Tables for *X*-Ray Crystallography,[4] and *R*, the usual discrepancy factor, was 0·44. A second Fourier series was summed, but the electron-density map did not reveal the final atom, and in fact suggested some errors in the location of the substituents of ring C; atom 16 (see Figure 1 for atom numbering) was rather poorly defined, and there was considerable electron density near atoms 16 and 6. The electron-density map was recalculated, with all the atoms of ring C omitted from the phasing, but this only confirmed the positions already deduced.

The positional and isotropic thermal parameters were then refined by (block-diagonal) least-squares, minimising $\Sigma w(|F|_o - |F_c|)^2$, with $\sqrt{w} = |F_o|/25$ when $|F_o| < 25$ and $\sqrt{w} = 25/|F_o|$ when $|F_o| \geqslant 25$. Four cycles reduced R to

---

[4] " International Tables for X-Ray Crystallography," vol. III, Kynoch Press, Birmingham, 1962.

0·34. The scale factor of each layer was then adjusted separately by application of the relation: $k|F_o| = |F_c| \exp\{\Delta B \,.\, \sin^2\theta/\lambda^2\}$, and a further three least-squares cycles reduced R to 0·26.

At this stage the intensities were measured with the counter equipment, and the analysis proceeded using the 798 reflexions with intensities greater than twice background. Since the measurements were reliable for all but the very weak reflexions, the weighting scheme used was $\sqrt{w} = 1$ when $|F_o| \geqslant 25$, $\sqrt{w} = |F_o|/25$ when $|F_o| < 25$. R was 0·196, and was reduced in two least-squares cycles to 0·170. At this stage three separate Fourier series were summed, with phases based on (i) all 28 atoms, (ii) all atoms except 5, 6, 16 (iii) atoms of the *p*-bromophenacyl group only. The three electron-density distributions were all very similar; they confirmed the positions of the atoms already found, and could best be interpreted by placing " half-atoms " at positions 16, 16′, 17, and 17′. Four further cycles of least-squares reduced R to 0·124. Attempts to refine structures with full atoms in any of the positions 16, 16′, 17, 17′ gave anomalously high thermal parameters for these atoms. The chemical nature of these " half-atoms " and the bond distances involving them (discussed later) indicate that they are oxygen atoms. A final set of structure factors was calculated for all planes with $2\theta(\text{Cu-}K_\alpha) \leqslant 102°$; the measured and calculated values for the 1379 planes are given in Table 1, R being 0·136 for the 984 observed reflexions. A final three-dimensional Fourier series was summed, and superimposed sections of the electron-density distribution taken through the atomic centres are shown, together with a perspective drawing of the structure, in Figure 1. The " half-oxygen " atoms are not as well resolved as Figure 1 indicates, since their densities are considerably drawn out in the *a*-direction.

TABLE 2

Fractional positional parameters and standard deviations (each × 10^4), isotropic thermal parameters and standard deviations (Å^2)

Atom	x	y	z	$\sigma(x)$	$\sigma(y)$	$\sigma(z)$	B	$\sigma(B)$
C(1)	3075	1321	3699	42	29	7	5·22	0·78
C(2)	1897	0751	4030	51	32	9	7·31	0·97
C(3)	3156	−0038	4357	50	35	8	7·20	0·91
C(4)	2486	−1616	4378	51	34	9	8·34	1·02
C(5)	0743	−1605	4624	63	40	10	11·58	1·27
C(6)	0540	−0289	4865	60	39	10	10·15	1·18
C(7)	2318	0539	4705	56	36	10	9·24	1·15
C(8)	1706	2176	4651	54	41	9	10·16	1·06
C(9)	0903	2118	4229	47	33	7	6·50	0·73
C(10)	1549	3437	4001	46	30	8	6·10	0·83
C(11)	1931	2801	3627	41	32	7	6·39	0·79
C(12)	0134	2253	3394	47	37	8	8·44	1·01
C(13)	3106	3672	3332	54	35	9	7·71	0·98
C(14)	3588	−2745	4215	63	43	10	12·09	1·21
C(15)	5639	0191	4297	61	41	10	10·74	1·20
O(16)	0717	−2896	4873	97	67	14	14·75	1·89
O(16′)	−0513	−2662	4651	73	55	13	11·39	1·51
O(17)	2428	0313	5019	80	53	13	9·88	1·52
O(17′)	3806	0370	5083	85	45	11	8·39	1·28
O(18)	−1641	2865	3434	32	23	5	8·67	0·60
O(19)	0076	1321	3114	31	23	5	7·00	0·60
C(20)	−1570	1042	2858	52	33	9	7·46	0·91
C(21)	−1798	2207	2584	48	37	8	8·05	0·93
O(22)	−0652	3260	2574	33	21	5	8·03	0·62
C(23)	−3560	2224	2321	42	31	7	5·45	0·71
C(24)	−5183	1121	2377	52	35	8	7·67	1·00
C(25)	−6745	1161	2121	47	32	8	6·42	0·84
C(26)	−6821	2062	1832	41	33	7	5·79	0·77
C(27)	−5166	3189	1768	43	32	8	6·21	0·84
C(28)	−3594	3129	2028	46	31	7	6·11	0·77
Br(29)	−8947	2132	1463	7	5	1	9·58	0·09

Refinement with visual data was completed by four more least-squares cycles, which reduced R to 0·214 for the 800 planes recorded on the films. These data are less accurate than the counter measurements, and the results did not differ significantly from those with the counter data. The visual structure factor data are not given here, but will be recorded.[5]

TABLE 3

Bond distances (Å) and valency angles (degrees). Standard deviations are about 0·05 Å and 3°

C(1)–C(2)	1·50	C(4)–C(14)	1·40
C(1)–C(11)	1·59	C(5)–O(16)	1·49
C(2)–C(3)	1·60	C(5)–O(16′)	1·29
C(2)–C(9)	1·59	C(6)–O(17)	1·46
C(3)–C(4)	1·54	C(7)–O(17)	1·13
C(3)–C(7)	1·45	C(7)–O(17′)	1·66
C(3)–C(15)	1·65	C(12)–O(18)	1·30
C(4)–C(5)	1·43	C(12)–O(19)	1·32
C(5)–C(6)	1·50	O(19)–C(20)	1·43
C(6)–C(7)	1·51	C(20)–C(21)	1·46
C(7)–C(8)	1·59	C(21)–O(22)	1·24
C(8)–C(9)	1·58	C(21)–C(23)	1·48
C(9)–C(10)	1·53	C(23)–C(24)	1·49
C(10)–C(11)	1·47	C(23)–C(28)	1·33
C(11)–C(12)	1·52	C(24)–C(25)	1·37
C(11)–C(13)	1·58	C(25)–C(26)	1·32
		C(26)–C(27)	1·53
		C(27)–C(28)	1·38
		C(26)–Br(29)	1·91
C(2)–C(1)–C(11)	101·1	C(8)–C(7)–O(17′)	109·5
C(1)–C(2)–C(3)	117·4	C(7)–C(8)–C(9)	99·3
C(1)–C(2)–C(9)	105·4	C(2)–C(9)–C(8)	107·7
C(3)–C(2)–C(9)	105·4	C(2)–C(9)–C(10)	107·7
C(2)–C(3)–C(4)	109·3	C(8)–C(9)–C(10)	112·0
C(2)–C(3)–C(7)	104·0	C(9)–C(10)–C(11)	101·0
C(2)–C(3)–C(15)	110·8	C(1)–C(11)–C(10)	106·7
C(4)–C(3)–C(7)	102·0	C(1)–C(11)–C(12)	99·0
C(4)–C(3)–C(15)	114·2	C(1)–C(11)–C(13)	111·8
C(7)–C(3)–C(15)	115·6	C(10)–C(11)–C(12)	119·2
C(3)–C(4)–C(5)	104·4	C(10)–C(11)–C(13)	116·3
C(3)–C(4)–C(14)	123·7	C(12)–C(11)–C(13)	102·3
C(5)–C(4)–C(14)	131·6	C(11)–C(12)–O(18)	118·9
C(4)–C(5)–O(16)	111·0	C(11)–C(12)–O(19)	130·4
C(6)–C(5)–O(16)	109·2	O(18)–C(12)–O(19)	110·2
C(4)–C(5)–C(6)	114·8	C(12)–O(19)–C(20)	127·9
C(4)–C(5)–O(16′)	123·1	O(19)–C(20)–C(21)	110·9
C(6)–C(5)–O(16′)	122·0	C(20)–C(21)–O(22)	123·4
C(5)–C(6)–C(7)	98·1	C(20)–C(21)–C(23)	120·1
C(5)–C(6)–O(17)	116·8	O(22)–C(21)–C(23)	116·4
C(7)–C(6)–O(17)	44·7	C(21)–C(23)–C(24)	117·5
C(6)–O(17)–C(7)	69·8	C(21)–C(23)–C(28)	120·3
C(6)–C(7)–O(17)	65·5	C(24)–C(23)–C(28)	122·0
C(3)–C(7)–C(6)	114·7	C(23)–C(24)–C(25)	115·1
C(3)–C(7)–C(8)	110·7	C(24)–C(25)–C(26)	123·7
C(3)–C(7)–O(17)	137·4	C(25)–C(26)–C(27)	121·7
C(3)–C(7)–O(17′)	115·0	C(25)–C(26)–Br(29)	125·1
C(6)–C(7)–C(8)	110·1	C(27)–C(26)–Br(29)	113·1
C(6)–C(7)–O(17′)	95·8	C(26)–C(27)–C(28)	113·8
C(8)–C(7)–O(17)	108·1	C(23)–C(28)–C(27)	123·5

At this point, the *X*-ray structure analysis was complete, and some chemical information was required to clarify the anomalies in the *X*-ray results. The original crystals were pure *p*-bromophenacyl ester, but the results of the *X*-ray analysis suggested that, after irradiation, there was a mixture of at least two compounds in the crystal, distributed randomly. Thus it appeared that the molecular structure, but not the crystal structure, was decomposing on exposure to *X*-rays. This suspicion was confirmed by irradiating samples of the derivative with unfiltered molybdenum radiation. After 10 hr. the decomposition was

---

[5] F. W. Comer, Ph.D. Thesis, University of British Columbia, 1966.

essentially complete, yielding a mixture of two compounds, which were separated by preparative thin-layer chromatography. One (40% yield) was the starting material, and the other (60% yield) was shown by i.r., n.m.r., and u.v. spectroscopy to be a rearranged product. As a final check, a single crystal was irradiated with Cu-K_α radiation under the conditions of intensity measurement, and this crystal when crushed showed depressed melting point, and gave two spots on thin-layer plates, which were consistent with the two spots obtained with the previously irradiated sample.

Two pieces of chemical evidence were now sufficient to fix the structures both of the *p*-bromophenacyl ester of hirsutic acid and of the rearrangement product: (i) the rearrangement product, but not the starting material, contains an α,β-unsaturated ketone system; (ii) each material contains one alcoholic function. The starting material is therefore (I; *R* = *p*-bromophenacyl) and the rearrangement product is (II; R = *p*-bromophenacyl) (the determination of the absolute configurations is described below).

Co-ordinates and Molecular Dimensions.—Only the parameters from the final least-squares cycle with the counter data are given, since these are the most accurate results. The final positional and isotropic thermal parameters are given in Table 2, together with their standard deviations calculated from the least-squares residuals.

The bond distances and valency angles are given in Table 3, and the shorter intermolecular distances in Table 4. The molecular packing, including possible hydrogen bonds, is illustrated in Figure 2.

The three five-membered rings were examined for planarity. The rings were all non-planar, and in each case it was found that one of the five possible four-atom planes was much better defined than the others, but only for the ring containing atoms 1, 2, 9, 10, 11 was an envelope conformation sharply defined. Table 5 summarises the equations of various planes (including the aromatic ring), deviations from the planes, and several pertinent dihedral angles.

TABLE 4

Shorter intermolecular distances

(All the crystallographically independent contacts $\leqslant 3{\cdot}70$ Å are listed)

Atom (Molecule 1)	to	Atom	in	Molecule	d (Å)
O(22)		C(25)		2	3·60
C(13)		O(18)		2	3·56
O(22)		C(20)		3	3·35
C(27)		C(1)		3	3·63
C(13)		C(24)		3	3·60
C(13)		C(25)		3	3·64
O(17)		O(16)		4	3·14
O(17)		O(16′)		4	3·05
C(7)		O(16)		4	3·64
C(4)		O(16)		4	3·41
C(5)		O(16′)		4	3·61
C(6)		O(16′)		4	3·64
C(15)		O(16)		4	3·63
C(14)		O(16)		4	3·55
O(16)		C(6)		4	3·70
O(16)		O(16)		4	3·47
O(16)		O(16′)		4	3·03
O(17′)		O(16)		4	2·63
O(17′)		O(16′)		4	2·74
O(17′)		C(9)		5	3·64
O(17′)		C(8)		5	3·12

Molecule	Co-ordinates
1	x, y, z
2	$1 + x, y, z$
3	$-x, \tfrac{1}{2} + y, \tfrac{1}{2} - z$
4	$\tfrac{1}{2} + x, -\tfrac{1}{2} - y, 1 - z$
5	$\tfrac{1}{2} + x, \tfrac{1}{2} - y, 1 - z$

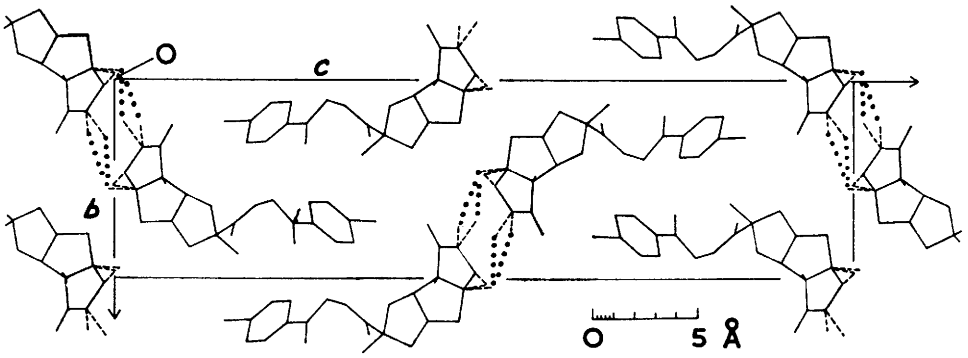


FIGURE 2 Projection of the structure along [100], illustrating the packing of the molecules and the hydrogen bonding between atom 17′ and atoms 16 or 16′:

○○○ hydrogen bonding between molecules
$x, 1 + y, z$ and $-\tfrac{1}{2} + x, \tfrac{1}{2} - y, 1 - z$
$1 - x, \tfrac{1}{2} + y, \tfrac{3}{2} - z$ and $\tfrac{1}{2} - x, -y, \tfrac{1}{2} + z$
$1 - x, \tfrac{1}{2} + y, \tfrac{1}{2} - z$ and $\tfrac{1}{2} - x, -y, -\tfrac{1}{2} + z$

●●● hydrogen bonding between molecules
$x, 1 + y, z$ and $\tfrac{1}{2} + x, \tfrac{1}{2} - y, 1 - z$
$1 - x, \tfrac{1}{2} + y, \tfrac{3}{2} - z$ and $\tfrac{3}{2} - x, -y, \tfrac{1}{2} + z$
$1 - x, \tfrac{1}{2} + y, \tfrac{1}{2} - z$ and $\tfrac{3}{2} - x, -y, -\tfrac{1}{2} + z$

Absolute Configuration.—As a final step in the analysis the absolute configurations of the molecules (both starting material and rearrangement product) were determined by the anomalous dispersion method.[6] Structure factors were calculated for all the *hkl* and $\bar{h}\bar{k}\bar{l}$ reflexions, using a scattering factor for Br of the form:

$$f = (f_{\mathrm{Br}} + \Delta f'_{\mathrm{Br}}) + i\,.\,\Delta f''_{\mathrm{Br}}$$

With Cu-K_α radiation the differences between $|F_c(hkl)|$ and $|F_c(\bar{h}\bar{k}\bar{l})|$ were quite small. The intensities for twelve sets of planes with relatively large differences were measured with the scintillation counter, and the results (Table 6) indicate unambiguously that the parameters used to calculate the structure factors (those of Table 2 referred to a conventional right-handed set of axes) represent the true absolute con-

---

[6] J. M. Bijvoet, A. F. Peerdeman, and A. J. van Bommel, *Nature*, 1951, **168**, 271.

TABLE 5

Equations of planes

Atoms in plane	Equation	Symbol
C(1)C(2)C(9)C(10)	$0{\cdot}8096\,X + 0{\cdot}0972\,Y + 0{\cdot}5788\,Z = 9{\cdot}2875$	(*A*)
C(3)C(2)C(9)C(8)	$0{\cdot}8051\,X + 0{\cdot}5230\,Y - 0{\cdot}2798\,Z = -\ 2{\cdot}6324$	(*B*)
C(4)C(5)C(6)C(7)	$-0{\cdot}5767\,X + 0{\cdot}3928\,Y - 0{\cdot}7163\,Z = -\ 12{\cdot}5574$	(*C*)
C(21)C(23)C(24)C(25)C(26)C(27)C(28)C(29)	$0{\cdot}4973\,X - 0{\cdot}6494\,Y - 0{\cdot}5753\,Z = -\ 7{\cdot}1831$	(*D*)

Deviations from mean planes (Å)

Atom	*A*	*B*	Atom	*C*	Atom	*D*
1	−0·0005	+	3	0·3646	21	0·0236
2	0·0007	0·0280	4	−0·0162	23	−0·0251
3	+	−0·0168	5	0·0255	24	0·0018
7		−0·5183	6	−0·0240	25	−0·0109
8	+	0·0117	7	0·0147	26	0·0021
9	−0·0007	−0·0223	14	−0·4348	27	−0·0144
10	0·0005	+	16′	0·0445	28	0·0066
11	−0·6196		16	−0·5247	29	0·0164

Dihedral angles (degrees)

Plane	Plane	ϕ
A	C(1)C(11)C(10)	42·8
A	*B*	122·7
B	C(3)C(7)C(8)	36·7
C	C(4)C(3)C(7)	22·8
C	C(6)O(17)C(7)	118·2
C(3)C(7) and C(2) or C(8)	C(3)C(7) and C(4) or C(6)	120 *

* An average of the four dihedral angles.

figuration. Figure 1 and (I) and (II) therefore depict the correct absolute configuration.

TABLE 6

Determination of the absolute configuration (Cu-K_{α} radiation)

h	k	l	$I_o(hkl)$	$I_o(\bar{h}\bar{k}\bar{l})$	$\lvert F_c(hkl)\rvert$	$\lvert F_c(\bar{h}\bar{k}\bar{l})\rvert$	$\dfrac{I_o(hkl)}{I_o(\bar{h}\bar{k}\bar{l})}$	$\dfrac{\lvert F_c(hkl)\rvert^2}{\lvert F_c(\bar{h}\bar{k}\bar{l})\rvert^2}$
1	1	2	4102	6057	57·6	65·2	0·68	0·78
1	1	11	338	273	19·9	16·9	1·24	1·39
1	2	5	2328	2220	54·3	50·3	1·05	1·17
1	2	8	4601	5223	82·6	86·4	0·88	0·91
1	2	16	30	46	5·9	8·6	0·65	0·47
1	3	1	173	106	14·4	10·1	1·63	2·03
1	3	2	814	714	41·2	37·3	1·14	1·22
1	3	8	225	164	26·0	22·2	1·37	1·37
1	3	12	267	328	24·4	27·9	0·81	0·77
2	1	6	205	108	12·7	9·2	1·90	1·91
2	1	8	226	168	17·8	15·0	1·35	1·41
2	3	4	773	572	37·4	33·6	1·35	1·24

DISCUSSION

The present *X*-ray analysis has established, with the assistance of some chemical evidence, the structure and absolute configuration of the *p*-bromophenacyl ester of hirsutic acid as (I; R = *p*-bromophenacyl). Hirsutic acid is therefore (I; R = H). The ester rearranges on irradiation with *X*-rays to form a product for which the *X*-ray analysis gives the structure and absolute configuration as (II; R = *p*-bromophenacyl). This rearrangement proceeds without disrupting the crystal structure, and produces only minor changes in lattice parameters and in the intensities of the reflexions. The crystal after irradiation contains the two different molecules distributed randomly at the lattice sites, since no superlattice reflexions or diffuseness were observed. Each atomic position determined by the *X*-ray analysis is therefore the mean of the positions in the separate molecules, which coincide very closely, except for the outer atoms in ring c. The relatively high thermal parameters (Table 2) are probably a result of this disorder rather than large vibrations, and these parameters are greatest in ring c, where the changes in atomic position in the rearrangement process are largest.

The general shapes of the molecules of the *p*-bromophenacyl ester of hirsutic acid, and of the rearrangement product, are clear from Figures 1 and 2. Table 5 defines the five-membered rings as envelopes or slightly distorted envelopes. Not too much significance should be attached to the detailed shape of ring c given in Table 5, as there are undoubtedly two centres at each atomic position, and only a mean position has been derived.

The measured bond distances and valency angles are not particularly accurate as a result of the disordered arrangement, but they are accurate enough to define unambiguously C(14) as an exocyclic methylene group, atom 16′ as a carbonyl oxygen and atom 16 as an alcohol function, atom 17 as an epoxide oxygen, and atom 17′ as a tertiary alcoholic function. These features and the two tertiary methyl groups are in agreement with other chemical and physical evidence.

The most significant intermolecular distances are O(17′) ··· O(16) and O(17′) ··· O(16′) contacts of 2·63 and 2·74 Å (Table 4), and these represent O–H ··· O hydrogen bonds. The original crystal does not contain any hydrogen bonds, since the shortest contact is O(16) ··· O(17) = 3·14 Å, and the nature of the hydrogen-bonding scheme formed during the irradiation-induced rearrangement probably has a strong influence on the rearrangement process. The rearrangement involves oxidation of the secondary alcoholic function on C(5) of hirsutic acid to a ketone, together with reduction of the epoxide ring, and the whole process appears to reach an equilibrium after about 60% of the original ester has undergone rearrangement. This could be explained on the basis of an intramolecular mechanism for any one molecule followed by hydrogen-bond formation between the newly-formed alcoholic group O(17′) and O(16) of a neighbouring unchanged molecule, thus stabilising that unchanged molecule. Since hydrogen bonds are also formed between O(17′) and O(16′), we should expect the rearrangement to proceed to somewhat more than 50% completion, since two neighbouring molecules could undergo rearrangement and still form a hydrogen bond between them. Whether the intramolecular mechanism, or some type of intermolecular route, is correct, the crystal packing and the formation of hydrogen bonds play an important role in the rearrangement. Irradiation of hirsutic acid itself resulted in no rearrangement, whereas irradiation of methyl hirsutate gave a rearrangement which is probably quite similar to the one observed with the *p*-bromophenacyl ester. In the free acid, hydrogen bonds involving the carboxyl group probably dominate the crystal packing.

All the other intermolecular distances in the crystal studied correspond to van der Waals interactions.

All the computations were carried out on the IBM 7040 computer with programmes of our own devising, and we are indebted to the staff of the University of British Columbia Computing Centre for assistance. We thank Professor A. I. Scott and Dr. F. McCapra for many helpful discussions, and the National Research Council of Canada for financial support and for the award of a research studentship (to F. W. C.).

DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF BRITISH COLUMBIA, VANCOUVER 8,
CANADA.
[5/673 *Received, June 28th*, 1965