

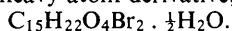
## The Crystal Structure and Absolute Configuration of 11,13-Dibromopulchellin

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The molecular structure and absolute configuration of pulchellin, a pseudoguaianolide sesquiterpene lactone, have been determined from its heavy-atom derivative, 11,13-dibromopulchellin,



The crystal belongs to the monoclinic system, space group  $P2_1$  with lattice constants:  $a = 10.28 \pm 0.02$ ,  $b = 22.55 \pm 0.04$ ,  $c = 8.19 \pm 0.01$  Å,  $\beta = 113^\circ 10' \pm 10'$ . The unit cell contains four molecules together with two molecules of water of crystallization. After refinement of atomic parameters by the block-matrix least-squares method allowing for anisotropic temperature factors, the final  $R$  index reached 0.106 for 1845 observed reflexions. The absolute configuration was determined from the anomalous dispersion. The two crystallographically independent molecules have nearly the same conformation. The bond lengths, angles and conformations are compared with those reported for other related sesquiterpene lactones. Within the crystal, the molecules are held together by several hydrogen bonds to form a double layer.

### Introduction

Puchellin [Fig. 1(a); Herz, Ueda & Inayama, 1963] and pulchellidine [Fig. 1(b); Yanagita, Inayama, Kawamata, Okura & Herz 1969] are the pseudoguaianolide sesquiterpene lactones isolated from *Gaillardia pulchella* Foug. The structure of pulchellidine was correlated to pulchellin by both degradative and synthetic methods (Yanagita *et al.*, 1969). Although structures for pulchellin and pulchellidine have been proposed on the basis of chem-

ical and spectroscopic data, some ambiguity remains concerning the stereochemistry of the ring junctions. We therefore decided to establish their stereostructure directly by X-ray analysis.

Preliminary accounts of the X-ray structure determination and the chemical study of pulchellin and pulchellidine have already been published (Sekita, Inayama & Iitaka, 1970; Yanagita, Inayama & Kawamata, 1970). While the manuscripts of the above communications were under preparation it became known that an American group had carried out an independent X-ray analysis of 3-bromoanhydrodehydrodihdropulchellin and had arrived at the same conclusion (Aota, Caughlan, Emerson, Herz, Inayama & Mazhar-Ul-Haque, 1970).\* However, their determination of the structure of pulchellin was based on the chemical transformation to 3-bromoanhydrodehydrodihdropulchellin, which did not reflect the exact stereochemistry of pulchellin and pulchellidine at the ring juncture because the chemical reaction to derive the 3-bromo derivative accompanies epimerization at atom C(1) together with the loss of the two asymmetric centres at atoms C(2) and C(4). Furthermore, the absolute configuration of pulchellin proposed by them was derived from a sequence of correlation between the stereostructures of bromoisotenulin, mexicanin I, aromatinin and pulchellin. The absolute configuration of bromoisotenulin taken as the basis of their study was not that determined by the X-ray method but that presumed on the basis of optical rotatory dispersion evidence (Herz, Romo de Vivar, Romo & Viswanathan, 1963).

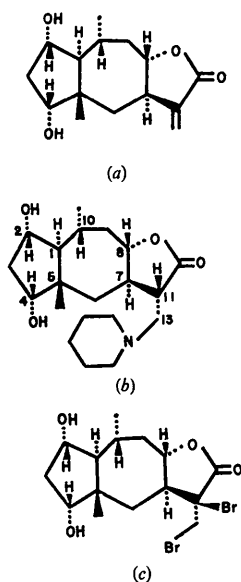


Fig. 1. Chemical structures. (a) Pulchellin, (b) pulchellidine, (c) 11,13-dibromopulchellin

\* Private communication from Professor W. Herz.

Table 1. The final atomic coordinates, thermal parameters and standard deviations

$x, y, z$  are the fractional coordinates. The temperature factors are expressed in the form  $T = \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ . The e.s.d.'s given in parentheses are in units of the least significant digits given for the corresponding parameters. To represent the correct absolute configuration, the coordinates should be referred to the left-handed coordinate system. Unprimed atoms belong to molecule I and a primed atoms to molecule II.

	$x$	$y$	$z$	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Br(11)	1-1115 (4)	0-1722 (0)	0-2179 (6)	0-0144 (5)	0-0029 (1)	0-0401 (11)	-0-0006 (2)	0-0139 (6)	0-0000 (3)
Br(13)	1-1062 (5)	-0-0179 (2)	0-4185 (7)	0-0256 (7)	0-0028 (1)	0-0388 (12)	0-0024 (2)	0-0176 (8)	0-0024 (3)
C(1)	0-6676 (25)	0-1202 (13)	0-4132 (38)	0-0054 (29)	0-0025 (7)	0-0188 (61)	-0-0000 (11)	0-0031 (32)	-0-0027 (17)
C(2)	0-5019 (33)	0-1055 (18)	0-3503 (39)	0-0113 (41)	0-0043 (11)	0-0131 (61)	-0-0005 (16)	0-0018 (37)	0-0008 (21)
C(3)	0-4456 (32)	0-0843 (19)	0-1629 (32)	0-0120 (41)	0-0056 (13)	0-0083 (50)	0-0006 (17)	-0-0026 (31)	-0-0023 (18)
C(4)	0-5611 (33)	0-0802 (18)	0-0998 (43)	0-0085 (39)	0-0045 (12)	0-0206 (73)	-0-0012 (16)	0-0026 (39)	-0-0024 (23)
C(5)	0-6680 (27)	0-1323 (15)	0-2263 (36)	0-0085 (33)	0-0035 (8)	0-0142 (57)	-0-0017 (13)	0-0082 (34)	-0-0042 (18)
C(6)	0-8089 (23)	0-1308 (17)	0-2041 (49)	0-0052 (25)	0-0039 (10)	0-0389 (93)	-0-0015 (12)	0-0082 (35)	-0-0028 (25)
C(7)	0-9385 (29)	0-1113 (20)	0-3839 (49)	0-0023 (30)	0-0063 (15)	0-0355 (94)	-0-0020 (16)	0-0140 (43)	-0-0038 (29)
C(8)	0-9653 (32)	0-1536 (16)	0-5175 (43)	0-0023 (30)	0-0028 (9)	0-0214 (71)	-0-0023 (15)	0-0067 (34)	-0-0035 (20)
C(9)	0-8914 (30)	0-1533 (18)	0-6608 (37)	0-0099 (37)	0-0050 (12)	0-0105 (56)	-0-0017 (16)	0-0035 (44)	-0-0044 (21)
C(10)	0-7313 (30)	0-1651 (14)	0-5520 (51)	0-0091 (35)	0-0021 (7)	0-0427 (100)	-0-0028 (14)	0-0096 (48)	-0-0039 (23)
C(11)	1-0737 (45)	0-1055 (13)	0-3664 (62)	0-0134 (42)	0-0091 (6)	0-0446 (119)	-0-0004 (16)	0-0098 (73)	-0-0004 (22)
C(12)	1-1840 (23)	0-1220 (17)	0-5581 (39)	0-0075 (25)	0-0052 (11)	0-0226 (67)	-0-0004 (12)	0-0040 (30)	-0-0034 (22)
C(13)	1-1022 (44)	0-0476 (15)	0-2501 (52)	0-0276 (70)	0-0021 (8)	0-0308 (96)	-0-0002 (18)	0-0161 (67)	0-0058 (22)
C(14)	0-6764 (30)	0-1634 (14)	0-7140 (33)	0-0140 (39)	0-0025 (7)	0-0092 (52)	-0-0008 (14)	0-0026 (35)	0-0012 (15)
C(15)	0-5713 (39)	0-1885 (17)	0-1084 (60)	0-0154 (51)	0-0030 (10)	0-0470 (127)	-0-0030 (17)	0-0138 (66)	0-0027 (27)
O(2)	0-4852 (34)	0-0604 (11)	0-4838 (43)	0-0019 (5)	0-0019 (5)	0-0471 (80)	-0-0004 (13)	0-0259 (54)	0-0004 (16)
O(4)	0-6480 (26)	0-0269 (10)	0-1521 (40)	0-0177 (37)	0-0021 (5)	0-0511 (82)	0-0010 (11)	0-0159 (45)	-0-0003 (17)
O(8)	1-1231 (19)	0-1523 (11)	0-6317 (26)	0-0084 (23)	0-0040 (7)	0-0187 (46)	-0-0007 (10)	-0-0003 (25)	-0-0030 (22)
O(12)	1-3112 (29)	0-1122 (18)	0-6061 (32)	0-0203 (43)	0-0088 (15)	0-0151 (51)	-0-0003 (20)	0-0103 (36)	-0-0026 (22)
Br(11')	-0-1030 (4)	0-3060 (2)	-0-0236 (5)	0-0155 (5)	0-0033 (1)	0-0248 (8)	-0-0009 (2)	0-0007 (5)	-0-0012 (0)
Br(13')	-0-1043 (5)	0-4999 (2)	0-1501 (5)	0-0216 (6)	0-0032 (1)	0-0245 (8)	0-0021 (2)	0-0058 (6)	0-0011 (2)
C(1')	0-3378 (27)	0-3659 (14)	0-6038 (37)	0-0084 (32)	0-0027 (8)	0-0151 (60)	-0-0004 (12)	0-0021 (33)	0-0031 (17)
C(2')	0-5024 (37)	0-3826 (19)	0-7173 (59)	0-0121 (48)	0-0036 (11)	0-0435 (119)	-0-0024 (18)	0-0127 (61)	0-0024 (28)
C(3')	0-5545 (30)	0-4097 (18)	0-5904 (37)	0-0074 (35)	0-0048 (11)	0-0108 (55)	-0-0002 (15)	-0-0005 (33)	0-0001 (20)
C(4')	0-4287 (27)	0-4046 (16)	0-4067 (42)	0-0036 (29)	0-0040 (10)	0-0206 (65)	-0-0007 (13)	-0-0049 (35)	-0-0002 (20)
C(5')	0-3376 (28)	0-3569 (14)	0-4103 (41)	0-0082 (33)	0-0022 (7)	0-0224 (67)	0-0010 (12)	-0-0017 (35)	0-0015 (18)
C(6')	0-1929 (36)	0-3549 (12)	0-2579 (43)	0-0198 (50)	0-0011 (5)	0-0238 (72)	-0-0003 (14)	0-0096 (48)	-0-0003 (16)
C(7')	0-0692 (29)	0-3660 (12)	0-3040 (48)	0-0078 (33)	0-0014 (6)	0-0371 (93)	-0-0000 (11)	0-0024 (44)	0-0003 (19)
C(8')	0-0333 (32)	0-3228 (14)	0-4379 (44)	0-0118 (41)	0-0024 (7)	0-0231 (76)	-0-0002 (13)	-0-0007 (42)	0-0021 (18)
C(9')	0-1125 (28)	0-3262 (10)	0-6186 (34)	0-0135 (37)	0-0035 (4)	0-0138 (54)	-0-0001 (10)	-0-0035 (33)	0-0012 (12)
C(10')	0-2718 (32)	0-3176 (17)	0-6774 (53)	0-0095 (38)	0-0028 (9)	0-0369 (99)	0-0007 (14)	0-0038 (47)	0-0001 (23)
C(11')	-0-0736 (33)	0-3719 (14)	0-1380 (44)	0-0142 (41)	0-0021 (7)	0-0241 (73)	-0-0012 (13)	0-0114 (45)	-0-0008 (18)
C(12')	-0-1753 (39)	0-3598 (15)	0-2258 (41)	0-0218 (54)	0-0022 (8)	0-0144 (63)	-0-0021 (17)	0-0020 (45)	-0-0008 (18)
C(13')	-0-0980 (26)	0-4238 (16)	0-0318 (35)	0-0069 (31)	0-0038 (9)	0-0109 (56)	0-0010 (13)	-0-0013 (31)	0-0058 (18)
C(14')	0-3363 (37)	0-2916 (34)	0-8989 (71)	0-0265 (84)	0-0090 (29)	0-0384 (133)	-0-0012 (39)	0-0190 (89)	0-0056 (50)
C(15')	0-4146 (34)	0-2966 (16)	0-4063 (49)	0-0137 (44)	0-0026 (8)	0-0291 (84)	0-0004 (15)	0-0041 (47)	-0-0009 (22)
O(2')	0-5113 (25)	0-4241 (12)	0-8698 (27)	0-0173 (33)	0-0037 (7)	0-0137 (43)	-0-0002 (12)	-0-0027 (29)	-0-0017 (14)
O(4')	0-3515 (22)	0-4605 (10)	0-3674 (35)	0-0104 (27)	0-0025 (5)	0-0439 (72)	-0-0008 (11)	0-0137 (36)	0-0006 (16)
O(8')	-0-1109 (20)	0-3339 (12)	0-3752 (30)	0-0084 (25)	0-0044 (8)	0-0270 (54)	-0-0008 (11)	0-0061 (28)	0-0030 (16)
O(12')	-0-3028 (21)	0-3697 (12)	0-1546 (30)	0-0090 (26)	0-0043 (8)	0-0234 (51)	-0-0010 (11)	0-0006 (28)	-0-0002 (16)
O(W')	0-1924 (32)	0-4895 (18)	0-0226 (45)	0-0236 (50)	0-0058 (11)	0-0495 (91)	0-0003 (21)	0-0073 (56)	0-0081 (28)



Table 2 (cont.)

-# 5 3	18.89	17.72	2 10 3	15.00	17.54	-4 14 4	18.58	22.77	8 10 4	7.34	9.29	8 2 5	10.85	10.44	-5 7 6	9.54	11.87	
-# 6 3	40.79	40.26	2 11 3	16.18	16.26	-4 15 4	13.76	19.39	-10 4 5	13.02	11.72	0 3 5	16.82	11.69	-5 8 6	15.42	12.47	
-# 7 3	28.11	26.62	2 12 3	16.93	16.93	-4 16 4	13.96	18.11	-10 5 5	20.14	20.49	0 4 5	7.60	7.92	-5 9 6	7.92	47.47	
-# 8 3	24.29	24.94	2 13 3	16.93	16.93	-4 17 4	9.15	4.11	-10 6 5	10.31	9.11	0 5 5	49.48	10.31	-5 10 6	15.18	11.81	
-# 9 3	29.08	30.74	2 14 3	9.47	10.23	-3 3 4	50.81	49.01	-10 12 5	9.39	12.38	0 6 5	47.40	40.14	-5 11 6	24.70	21.90	
-# 10 3	9.42	9.02	2 15 3	17.07	17.07	-3 4 4	11.81	11.81	-10 13 5	10.49	10.49	0 7 5	26.27	26.04	-5 12 6	13.63	14.72	
-# 11 3	36.96	39.26	2 16 3	15.63	13.31	-3 5 4	2.11	7.00	-10 14 5	31.85	29.30	0 8 5	10.62	17.70	-5 13 6	10.62	17.70	
-# 12 3	12.44	13.43	2 17 3	9.00	12.74	-3 6 4	69.03	48.87	-9 1 5	30.45	26.71	0 9 5	21.22	15.73	-4 1 5	14.48	10.34	
-# 13 3	13.16	17.14	2 18 3	17.07	17.07	-3 7 4	26.83	17.07	-9 2 5	46.32	17.20	0 10 5	32.17	32.14	-4 2 5	12.17	12.14	
-# 14 3	23.71	25.31	3 1 3	20.65	40.87	-3 8 4	12.10	12.11	-9 3 5	16.25	13.30	0 11 5	8.71	7.08	-4 3 5	10.40	7.40	
-# 15 3	7.55	27.37	3 2 3	40.92	47.42	-3 9 4	40.92	47.42	-9 4 5	19.79	20.94	0 12 5	13.41	11.92	-4 4 5	20.62	18.98	
-# 16 3	13.87	10.92	3 3 3	3 3	10.92	-3 10 4	11.81	11.81	-9 5 5	18.89	14.29	0 13 5	18.34	17.93	-4 5 5	12.35	9.72	
-# 17 3	31.51	20.71	3 4 3	33.16	31.93	-3 11 4	31.25	34.71	-9 6 5	14.27	12.79	0 14 5	11.11	14.90	-4 6 5	18.67	16.50	
-# 18 3	16.49	16.49	3 5 3	16.49	16.49	-3 12 4	16.49	16.49	-9 7 5	18.49	7.31	0 15 5	9.70	5.40	-4 7 5	12.40	10.00	
-# 19 3	52.57	40.67	3 6 3	34.73	31.17	-3 13 4	9.32	13.41	-9 8 5	10.79	11.37	0 16 5	10.79	5.40	-4 8 5	17.30	14.21	
-# 20 3	54.15	51.03	3 7 3	42.56	42.34	-3 14 4	32.11	39.08	-9 9 5	9.42	10.44	0 17 5	4.65	0.00	-4 9 5	14.36	15.00	
-# 21 3	53.49	48.98	3 8 3	23.97	42.31	-3 15 4	14.84	21.07	-9 10 5	7.28	7.34	0 18 5	4.65	0.00	-4 10 5	18.13	20.85	
-# 22 3	45.80	40.49	3 12 3	50.07	39.77	-3 16 4	14.84	21.07	-9 11 5	27.00	23.02	0 19 5	1.4	54.77	49.40	-4 11 5	15.96	14.42
-# 23 3	52.24	53.18	3 13 3	24.54	49.51	-3 17 4	9.31	9.44	-9 12 5	17.30	14.59	0 20 5	15.29	10.05	-4 12 5	15.96	14.42	
-# 24 3	27.07	27.99	3 14 3	16.67	17.13	-3 18 4	11.77	11.73	-9 13 5	10.79	9.90	0 21 5	10.79	9.90	-4 13 5	11.81	11.29	
-# 25 3	26.31	24.46	3 25 3	5.00	5.04	-3 20 4	10.25	10.44	-8 4 5	17.06	10.48	1 4 5	7.31	0.00	-4 14 5	11.75	11.48	
-# 26 3	23.87	24.40	4 1 3	16.15	11.10	-3 22 4	8.01	8.44	-8 5 5	30.67	36.17	1 5 5	57.10	49.05	-4 15 5	12.22	11.40	
-# 27 3	16.47	16.07	4 2 3	34.74	30.37	-2 1 4	34.74	30.37	-8 6 5	10.99	13.15	1 6 5	7.92	9.55	-4 16 5	12.22	11.40	
-# 28 3	35.46	39.16	4 3 3	15.84	14.40	-2 2 4	48.37	42.31	-8 7 5	9.12	9.96	1 7 5	22.89	22.70	-4 17 5	7.31	8.88	
-# 29 3	27.70	30.01	4 4 3	26.57	26.69	-2 3 4	72.07	75.92	-8 8 5	12.30	14.90	1 8 5	8.20	6.79	-4 18 5	23.89	18.43	
-# 30 3	8.55	4.54	4 5 3	17.33	19.04	-2 4 4	9.57	86.14	-8 9 5	25.21	24.35	1 9 5	41.81	42.16	-4 19 5	4.98	2.83	
-# 31 3	13.31	13.71	4 6 3	19.81	19.81	-2 5 4	21.71	21.30	-8 10 5	8.85	9.10	1 10 5	8.85	9.48	-4 20 5	13.68	12.45	
-# 32 3	8.61	7.55	4 7 3	24.13	27.64	-2 6 4	10.77	10.90	-8 11 5	5.30	6.29	1 11 5	10.09	10.29	-4 21 5	17.99	17.48	
-# 33 3	8.93	3.23	4 8 3	30.76	42.17	-2 7 4	47.27	49.09	-8 12 5	8.43	9.45	1 12 5	11.33	11.46	-4 22 5	13.60	12.45	
-# 34 3	70.87	60.49	4 9 3	10.76	11.50	-2 8 4	16.10	11.42	-8 13 5	12.50	8.64	1 13 5	15.27	5.08	-4 23 5	11.81	11.47	
-# 35 3	40.42	30.41	4 10 3	14.84	14.34	-2 9 4	37.63	47.61	-7 1 5	30.96	34.28	1 14 5	12.83	17.87	-4 24 5	21.77	21.21	
-# 36 3	40.80	40.43	4 11 3	16.18	16.26	-2 10 4	19.29	29.20	-7 2 5	16.18	13.24	1 15 5	33.70	43.79	-4 25 5	11.04	12.44	
-# 37 3	41.46	40.74	4 12 3	16.18	16.26	-2 11 4	7.48	7.48	-7 3 5	19.30	19.77	1 16 5	19.37	19.77	-4 26 5	11.04	12.44	
-# 38 3	62.08	62.79	5 0 3	26.71	42.27	-2 12 4	13.05	10.50	-7 4 5	18.10	17.03	2 2 5	10.45	15.27	-4 27 5	25.18	22.72	
-# 39 3	53.49	48.98	5 1 3	17.07	17.07	-2 13 4	19.02	19.02	-7 5 5	29.04	29.84	2 3 5	19.63	19.63	-4 28 5	16.46	21.51	
-# 40 3	73.09	75.08	5 2 3	44.30	39.74	-2 14 4	19.25	42.50	-7 6 5	18.05	15.27	2 4 5	15.45	15.20	-4 29 5	12.22	11.40	
-# 41 3	49.80	49.49	5 3 3	17.04	11.59	-2 15 4	8.87	11.24	-7 7 5	10.28	14.80	2 5 5	43.69	30.92	-4 30 5	12.22	11.40	
-# 42 3	27.49	26.64	5 4 3	7.91	47.79	-2 16 4	14.40	14.40	-7 8 5	12.40	14.74	2 6 5	10.79	10.79	-4 31 5	10.80	10.80	
-# 43 3	23.87	24.40	5 5 3	9.36	10.30	-2 17 4	4.10	11.24	-7 9 5	10.28	14.80	2 7 5	17.14	10.32	-4 32 5	9.51	9.54	
-# 44 3	16.47	16.07	5 6 3	16.47	16.07	-2 18 4	11.11	11.11	-7 10 5	13.34	13.90	2 8 5	8.45	19.35	-4 33 5	9.29	7.56	
-# 45 3	35.46	39.16	5 7 3	27.34	26.43	-2 19 4	6.13	16.37	-7 11 5	11.81	11.81	2 9 5	11.81	11.81	-4 34 5	11.81	11.81	
-# 46 3	17.09	13.37	5 8 3	30.30	32.25	-1 0 4	13.03	30.70	-7 12 5	9.58	0.93	2 10 5	10.53	20.49	-4 35 5	35.02	36.83	
-# 47 3	27.70	30.01	5 9 3	30.30	32.25	-1 1 4	8.01	13.83	-7 13 5	9.22	18.42	2 11 5	12.12	12.08	-4 36 5	11.79	14.87	
-# 48 3	23.27	24.63	5 10 3	16.66	17.63	-1 2 4	39.53	39.44	-6 0 5	66.80	64.92	2 12 5	10.12	6.09	-4 37 5	11.79	14.87	
-# 49 3	18.17	17.25	5 11 3	15.06	21.20	-1 3 4	90.14	91.90	-6 1 5	18.99	10.44	2 13 5	8.08	7.00	-4 38 5	3.86	6.99	
-# 50 3	12.42	12.42	5 12 3	12.42	12.42	-1 4 4	48.14	48.14	-6 2 5	12.70	19.77	2 14 5	10.79	10.79	-4 39 5	11.79	14.87	
-# 51 3	7.21	6.49	5 13 3	14.78	19.32	-1 5 4	29.13	19.14	-6 3 5	24.95	44.10	2 15 5	7.63	7.00	-4 40 5	24.87	25.47	
-# 52 3	99.83	90.85	5 14 3	7.98	0.80	-1 6 4	28.70	42.50	-6 4 5	21.67	21.36	2 16 5	7.63	7.00	-4 41 5	16.60	12.43	
-# 53 3	70.29	60.49	5 15 3	10.76	10.76	-1 7 4	10.76	10.76	-6 5 5	4.25	4.25	2 17 5	7.15	7.15	-4 42 5	16.60	12.43	
-# 54 3	19.50	20.97	5 16 3	18.79	16.73	-1 8 4	18.79	16.73	-6 6 5	7.95	8.63	3 1 5	40.09	41.21	-4 43 5	24.61	24.10	
-# 55 3	19.50	20.97	5 17 3	18.79	16.73	-1 9 4	18.79	16.73	-6 7 5	18.16	19.03	3 2 5	15.72	11.67	-4 44 5	18.48	13.57	
-# 56 3	27.64	28.97	5 18 3	19.50	19.50	-1 10 4	29.00	31.54	-6 8 5	16.16	19.03	3 3 5	10.92	9.48	-4 45 5	11.81	11.47	
-# 57 3	6.25	6.25	5 19 3	16.70	20.61	-1 11 4	21.70	18.34	-6 9 5	26.40	28.00	3 4 5	23.78	20.63	-4 46 5	12.77	15.77	
-# 58 3	36.10	40.43	5 20 3	25.76	27.77	-1 12 4	24.74	21.30	-6 10 5	26.40	28.00	3 5 5	23.78	20.63	-4 47 5	11.81	11.47	
-# 59 3	6.25	6.25	5 21 3	16.66	17.22	-1 13 4	19.29	29.47	-6 11 5	10.12	11.10	3 6 5	39.00	41.33	-4 48 5	14.07	14.47	
-# 60 3	25.76	23.63	5 22 3	12.42	12.42	-1 14 4	14.52	14.52	-6 12 5	12.12	11.10	3 7 5	12.12	11.10	-4 49 5	14.07	14.47	
-# 61 3	10.69	17.38	5 23 3	16.31	16.77	-1 15 4	16.16	10.50	-6 13 5	15.93	17.07	3 8 5	32.35	30.17	-4 50 5	9.22	6.72	
-# 62 3	17.09	16.03	5 24 3	16.31	16.77	-1 16 4	11.11	11.10	-6 14 5	4.35	6.10	3 9 5	21.48	20.43	-4 51 5	21.48	20.43	
-# 63 3	49.20	39.74	5 25 3	16.77	16.77	-1 17 4	12.49	11.10	-6 15 5	21.63	12.94	3 10 5	19.63	19.63	-4 52 5	19.63	19.63	
-# 64 3	26.20	24.00	5 26 3	9.89	9.42	-1 18 4	11.10	11.10	-6 16 5	6.83	6.48	3 11 5	9.89	9.42	-4 53 5	18.77	15.61	
-# 65 3	15.14	13.14	5 27 3	18.79	16.73	-1 19 4	18.79	16.73	-6 17 5	50.06	40.32	3 12 5	11.68	10.37	-4 54 5	21.43	19.26	
-# 66 3	4.70	4.70	5 28 3	10.18	10.30	0 0 4	42.10	40.69	-6 18 5	17.16	14.22	3 13 5	10.79	10.79	-4 55 5	11.81	11.47	
-# 67 3	28.29	34.29	5 29 3	10.18	10.30	0 1 4	10.18	40.69	-6 19 5	11.05	18.05	3 14 5	15.16	18.05	-4 56 5	16.56	19.74	
-# 68 3	11.23	12.27	5 30 3	10.18	10.30	0 2 4	27.23	27.52	-6 20 5	17.43	10.57	3 15 5	19.37	13.10	-4 57 5	11.81	11.47	
-# 69 3	18.11	16.91	5 31 3	9.89														

In view of this, the present study of 11,13-dibromopulchellin [Fig. 1(c)] is clearly more suitable for the structure determination of pulchellin and pulchellidine, because the compound is derived from the original sesquiterpene lactones with only minor structural changes, in which the bromination reaction at atom C(11) occurs stereospecifically as in the addition reaction of piperidine to pulchellin, and this makes it possible to deduce the configuration at atom C(11) of pulchellidine.

### Experimental

After unsuccessful attempts to prepare several derivatives of pulchellin and pulchellidine only 11,13-dibromopulchellin [Fig. 1(c)] proved to be suitable for X-ray analysis. The bromination of pulchellin was carried out by adding equimolar quantities of bromine to the chloroform solution of pulchellin. After evaporation of the solvent, the remaining crystalline mass was triturated with chloroform and ether to give prismatic crystals, m.p. 110–113°C. Recrystallization from the same solvent mixture afforded giant prisms, m.p. 113–115°C.

*Analysis:*  $C_{15}H_{22}O_4Br_2 \cdot \frac{1}{2}H_2O$ . Calculated: C, 41.4; H, 5.3. Found: C, 42.7; H, 4.8. Ultraviolet spectrum (EtOH): end absorption. Infrared spectrum (KBr): 3476(OH), 3556(OH) and  $1774\text{ cm}^{-1}$  ( $\gamma$ -lactone).

The crystals were colourless monoclinic prisms well developed along the *c* axis. The unit-cell dimensions and space group were determined from precession photographs of layers *0kl*, *h0l* and *hk0* taken with Cu *K* $\alpha$  radiation. The crystal density measured by the flotation method in mixtures of carbon tetrachloride and methyl iodide was  $1.65_3\text{ g. cm}^{-3}$ . The density was calculated to be  $1.656\text{ g. cm}^{-3}$  assuming that four molecules of dibromopulchellin and two water molecules are contained in the unit cell. The existence of water of crystallization was confirmed by nuclear magnetic resonance spectra and the amount of water estimated by the weight loss of the crystals upon heating corresponded to 93% of the formulated water content.

### Crystal data

11,13-dibromopulchellin hemihydrate,  
 $C_{15}H_{22}O_4Br_2 \cdot \frac{1}{2}H_2O$ , m.p. 113–115°C, F.W. 435

Monoclinic

$$a = 10.28 \pm 0.02, \quad b = 22.55 \pm 0.04,$$

$$c = 8.19 \pm 0.01 \text{ \AA},$$

$$\beta = 113^\circ 10' \pm 10',$$

$$V = 1745 \text{ \AA}^3$$

$$D_m = 1.65_3, \quad D_x = 1.656 \text{ g. cm}^{-3},$$

$$Z = 4,$$

$$F(000) = 876$$

Absent spectra: *0k0* when *k* is odd.

Space group:  $P2_1$

Intensity data were recorded on multiple-film equi-inclination Weissenberg photographs taken with Cu *K* $\alpha$

radiation. Layer lines of zero to six around *c* and zero to three around the *b* axis were recorded. The intensities were estimated visually with the aid of intensity scales. The values were corrected for the usual Lorentz and polarization factors, but not absorption. A total of 1845 independent observed structure factors were derived by correlating the equivalent structure factors recorded on various layers.

### Determination of the structure

The crystal structure was solved by the heavy-atom method. The positions of the four independent bromine atoms were determined from a three-dimensional Patterson map. Successive use of Fourier and difference Fourier synthesis revealed all the atomic positions of the two independent molecules and the water molecule. Refinement of the atomic parameters was carried out by several cycles of block-matrix least-squares calculations (program by Okaya & Ashida, 1967) allowing for the anisotropic thermal motion of each atom. The final value of the *R* index for 1845 reflexions was 0.106. The following weighting system was adopted in the least-squares calculation

$$\begin{cases} w = 28/F_o, & \text{when } 28 < F_o \\ w = 1.0 & \text{when } 3 < F_o \leq 28, \\ w = 0 & \text{when } F_o \leq 3. \end{cases}$$

The atomic scattering factors used were those given by Berghuis, Haanappel, Potters, Loopstra, MacGillivray & Veenendaal (1955) for carbon and oxygen and those given by Thomas & Umeda (1957) for bromine. The final atomic parameters and their standard deviations are listed in Table 1, and the list of the observed and calculated structure factors is given in Table 2.

Table 3. Comparison of the calculated and observed intensity ratios of the Friedel pairs of reflexions used for the establishment of the absolute configuration

<i>h</i>	<i>k</i>	<i>l</i>	$ F_o(hkl) ^2/ F_o(h\bar{k}l) ^2$	$I_o(hkl)/I_o(h\bar{k}l)$
3	6	0	0.92	< 1
3	9	0	1.65	> 1
5	1	0	1.40	> 1
5	1	1	0.82	< 1
2	4	1	0.88	< 1
2	5	1	1.29	> 1
3	6	1	0.88	< 1
4	5	1	1.26	> 1
0	1	2	0.81	< 1
5	1	2	0.86	< 1
5	5	2	1.47	> 1
6	4	2	0.72	< 1
5	2	3	0.82	< 1
2	5	3	1.14	> 1
5	2	4	0.88	< 1
1	1	4	1.48	> 1
0	4	4	0.75	< 1
3	1	4	1.34	> 1
1	4	6	1.25	> 1

The absolute configuration of the molecules was established from the anomalous dispersion of Cu *K* $\alpha$

Table 4. Bond angles and distances involved in the hydrogen-bonded groups

Unprimed atoms belong to molecule I and primed atoms to molecule II.

	Angle		Distance
C(12')-O(12')-O(2')	140°	O(12')-O(2')	2.66 Å
O(12')-O(2')-C(2')	103		
O(12')-O(2')-O(4)	130	O(2')-O(4)	2.80
C(2')-O(2')-O(4)	127		
O(2')-O(4)-C(4)	113		
O(2')-O(4)-O(W)	100	O(4)-O(W)	2.70
C(4)-O(4)-O(W)	122		
O(4)-O(W)-O(4')	112		
O(W)-O(4')-C(4')	119		
O(W)-O(4')-O(2)	106	O(W) · O(4')	2.73
C(4')-O(4')-O(2)	115		
O(4')-O(2)-C(2)	129		
O(4')-O(2)-O(12)	125	O(4')-O(2)	2.79
C(2)-O(2)-O(12)	105		
O(2)-O(12)-C(12)	139	O(2)-O(12)	2.64
Standard deviation	1-3°		0.03-0.05 Å

radiation by the bromine atom. The values of the dispersion correction terms,  $\Delta f' = -0.9$  and  $\Delta f'' = 1.5$  were taken from *International Tables for X-ray Crystallography* (1962). The nineteen sets of reflexions for which the intensity ratios of the  $hkl$  and  $h\bar{k}l$  reflexions were calculated to be significantly different from unity clearly showed intensity differences on the  $c$ -axis Weissenberg photographs in agreement with the calculated values. A comparison of the calculated and observed intensity ratios of the Friedel pairs of reflexions from which the absolute configuration was established are shown in Table 3. All Figures of 11,13-dibromopulchellin shown in the present paper are drawn with the correct absolute configuration.

### Results and discussion

Projections of the two molecules, I and II, along the  $b$  and  $c$  axes are shown in Figs. 2 and 3 respectively.

Although these two molecules are crystallographically independent, they take almost the same conformation. Furthermore, they are situated as if they were related by a pseudo-twofold screw axis lying parallel to the  $c$  axis. There are several hydrogen bonds between the molecules, as shown by the dotted lines in Figs. 3 and 4. The lengths and angles of these bonds are listed in Table 4. It will be seen that the molecules in the crystal form complex nets of double layers. The intermolecular distances less than 4.0 Å, except the hydrogen bonds, are listed in Table 5.

Table 5. Intermolecular distances less than 4.0 Å excluding hydrogen bonds

Unprimed atoms belong to molecule I and primed atoms to molecule II.

	Distance	Symmetry
Br(11)-Br(11')	3.80 Å	3
Br(15)-Br(15')	3.56	6

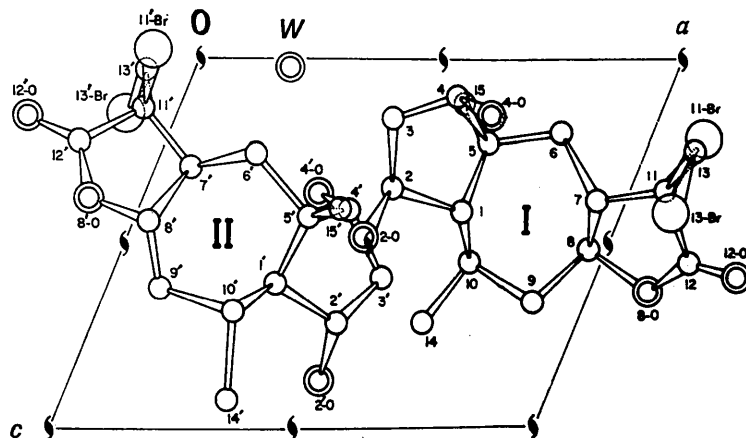
Fig. 2.  $b$  axis projection of the crystal structure. Coordinates of atoms of molecules I and II are given in Table 1.

Table 5 (cont.)

	Distance	Symmetry
Br(15)—C(3')	3.86	7
Br(15)—C(12')	3.87	6
Br(15)—C(15')	3.88	4
Br(15)—O(8')	3.74	6
Br(15)—O(W)	3.71	4

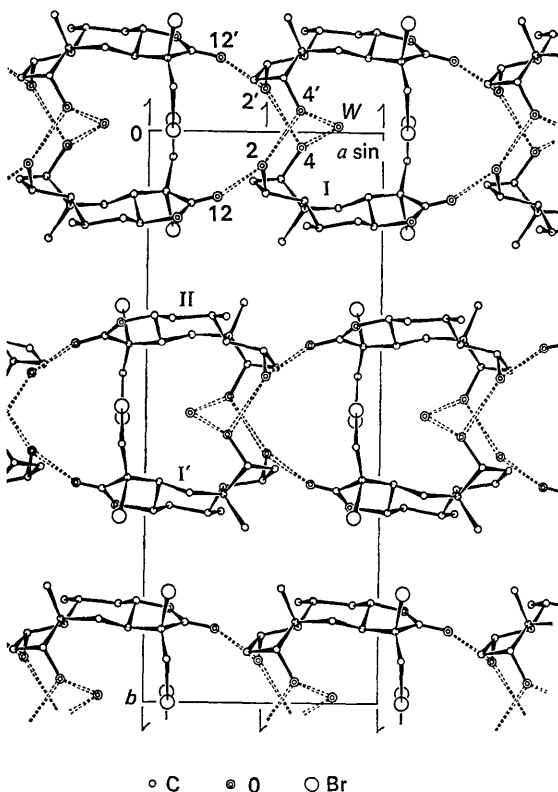
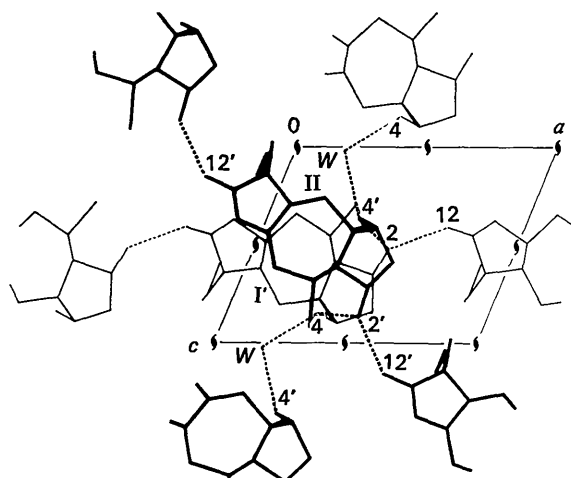

 Fig. 3. *c*-axis projection of the crystal structure. Dotted lines indicate hydrogen bonds.

 Fig. 4. Network of hydrogen bonds shown in *b*-axis projection. The molecules denoted by I' and II correspond to those in Fig. 3.

Table 5 (cont.)

C(2)—O(12)	3.39	3
C(2)—O(4')	3.95	6
C(3)—Br(15')	3.93	2
C(3)—C(15)	3.96	3
C(3)—O(2')	3.66	6
C(4)—O(12)	3.91	5
C(4)—O(2')	3.63	6
C(4)—O(W)	3.69	4
C(6)—O(W)	3.69	4
C(8)—C(8')	3.77	3
C(8)—C(9')	3.93	3
C(12)—Br(15')	3.94	6
C(12)—O(2)	3.66	3
C(13)—O(12)	3.69	3
C(15)—Br(15')	3.46	4
C(15)—C(15')	3.61	4
C(15)—O(2)	3.65	3
C(15)—O(W)	3.25	4
O(2)—C(3')	3.45	6
O(2)—C(4')	3.65	6
O(4)—C(2')	3.93	6
O(8)—Br(15')	3.91	6
O(8)—C(9')	3.92	3
O(8)—C(10')	3.99	3
Br(15')—O(W)	3.60	1
C(2')—O(12')	3.36	5
C(3')—C(15')	3.97	5
C(4')—O(W)	3.67	1
C(6')—O(W)	3.59	1
C(12')—O(2')	3.69	5
C(13')—O(12')	3.64	5
C(15')—O(2')	3.70	5
C(15')—O(W)	3.36	1

Symmetry:

1	$x, y, z$
2	$-x, \frac{1}{2}y, -z$
3	$1+x, y, z$
4	$1-x, \frac{1}{2}y, -z$
5	$1+x, y, 1+z$
6	$1-x, \frac{1}{2}y, 1-z$
7	$2-x, \frac{1}{2}y, 1-z$

The bond lengths and angles found in the present molecules are listed in Tables 6 and 7, in which their values are compared with those reported for other pseudoguaianolide derivatives: 3-bromoanhydrodehydrodihydropulchellin (Aota *et al.*, 1970), bromohelenalin (Mazhar-Ul-Haque & Caughlan, 1969) and bromomexicanin-E (Mazhar-Ul-Haque & Caughlan, 1967). Although the bond lengths and angles found in the present molecules are consistent with the chemical formula, some of the values differ significantly from those reported for analogous compounds. There are also some differences between molecules I and II in the present crystal. Most of the differences are, however, within the limits of experimental error and it seems to be unrealistic to discuss the differences at present, since the standard deviations of the atomic parameters in the present analysis are rather large.

The conformations of the molecules found in various pseudoguaianolides are illustrated in Fig. 5. It is of interest to note that although rings *A* and *C* are fused to the *B* ring in different ways and the overall conformations of the molecules are different, the seven-membered *B* rings take similar conformations.

As seen in Figs 2, 3 and 5, the stereochemistry of the present molecule is established as follows:

C(5)- $\beta$ CH<sub>3</sub> is *trans* to C(1)- $\alpha$ H forming a *trans* ring junction of the cyclopentanedial ring to the seven-membered ring.

C(7)- $\alpha$ H is *trans* to C(8)- $\beta$ H forming a *trans*-fused  $\gamma$ -lactone ring.

C(2)- $\beta$ H is *cis* to C(4)- $\beta$ H forming a *cis* 1,3-diol.

C(10)- $\alpha$ CH<sub>3</sub> is *cis* to C(1)- $\alpha$ H.

C(11)- $\alpha$ CH<sub>2</sub>Br is *cis* to C(7)- $\alpha$ H.

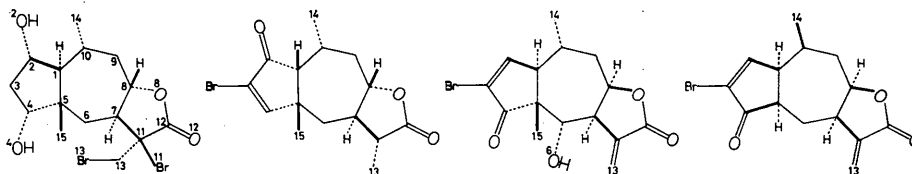
C(11)- $\beta$ Br is *trans* to C(13)-Br.

The present study on 11,13-dibromopulchellin has established the absolute configuration of pulchellin in a direct way and the result obtained coincides with that

Table 6. Comparison of bond lengths found in various pseudoguaianolide derivatives

	11,13-Dibromopulchellin		3-Bromoanhydrodehydrodihydro-pulchellin		Bromohele-nalin	Bromo-mexicanin-E
	I	II	I	II		
C(1)—C(2)	1.61 (0.04) Å	1.62 (0.04) Å	1.57 Å	1.58 Å	1.51 Å	1.49 Å
C(1)—C(5)	1.56 (0.05)	1.60 (0.05)	1.52	1.57	1.54	1.54
C(1)—C(10)	1.47 (0.04)	1.53 (0.05)	1.54	1.50	1.55	1.59
C(2)—C(3)	1.49 (0.04)	1.48 (0.06)	1.47 <sup>a</sup>	1.45 <sup>a</sup>	1.31 <sup>b</sup>	1.32 <sup>b</sup>
C(2)—O(2)	1.55 (0.05) <sup>c</sup>	1.53 (0.05) <sup>c</sup>	1.17 <sup>e</sup>	1.18 <sup>e</sup>		
C(3)—C(4)	1.47 (0.05)	1.56 (0.04)	1.33 <sup>b</sup>	1.34 <sup>b</sup>	1.45 <sup>a</sup>	1.46 <sup>a</sup>
C(3)—Br			1.91	1.89	1.89	1.92
C(4)—C(5)	1.66 (0.05)	1.43 (0.05)	1.53	1.55	1.55	1.51
C(4)—O(4)	1.46 (0.04) <sup>c</sup>	1.46 (0.04) <sup>c</sup>			1.21 <sup>e</sup>	1.22 <sup>e</sup>
C(5)—C(6)	1.53 (0.04)	1.52 (0.04)	1.52	1.57	1.52	1.56
C(5)—C(15)	1.67 (0.05)	1.58 (0.05)	1.55	1.53	1.54	
C(6)—C(7)	1.61 (0.04)	1.48 (0.06)	1.54	1.54	1.57	1.54
C(6)—O(6)					1.44 <sup>c</sup>	
C(7)—C(8)	1.56 (0.06)	1.61 (0.05)	1.54	1.51	1.54	1.56
C(7)—C(11)	1.46 (0.06)	1.57 (0.04)	1.58	1.52	1.51	1.51
C(8)—C(9)	1.65 (0.05)	1.38 (0.04)	1.48	1.48	1.52	1.50
C(8)—O(8)	1.54 (0.03)	1.39 (0.04)	1.41	1.49	1.50	1.47
C(9)—C(10)	1.56 (0.04)	1.53 (0.04)	1.57	1.54	1.56	1.55
C(10)—C(14)	1.63 (0.06)	1.67 (0.07)	1.57	1.58	1.52	1.53
C(11)—C(12)	1.58 (0.05)	1.51 (0.06)	1.58	1.51	1.52	1.55
C(11)—C(13)	1.71 (0.06)	1.42 (0.05)	1.53	1.60	1.31 <sup>b</sup>	1.34 <sup>b</sup>
C(11)—Br(11)	2.07 (0.05)	1.93 (0.03)				
C(12)—O(8)	1.23 (0.04)	1.28 (0.04)	1.29	1.32	1.33	1.33
C(12)—O(12)	1.23 (0.04) <sup>e</sup>	1.23 (0.04) <sup>e</sup>	1.28 <sup>e</sup>	1.25 <sup>e</sup>	1.21 <sup>e</sup>	1.22 <sup>e</sup>
C(13)—Br(13)	2.01 (0.04)	1.98 (0.03)				
Standard deviation	in parentheses		±0.01—0.02	±0.01—0.02	±0.01—0.03	
Mean C—C	1.55		1.54	1.54	1.54	
Mean C=C			1.34	1.31	1.33	
Mean C—OH	1.50			1.44		
Mean C=O	1.23		1.22	1.21	1.22	
Mean C—Br	2.00		1.90	1.89	1.92	
Number of reflexions	1845 <sup>v</sup>		2376 <sup>d</sup>	1125 <sup>d</sup>	750 <sup>d</sup>	800 <sup>v</sup>
R index (%)	10.6		6.6	5.8	6.2	

Formula



Ring conformation

Somewhat deformed flat chair

Somewhat deformed chair

Deformed chair

Boat

AB junction  
BC junction

*trans*  
*trans*

*cis*  
*trans*

*trans*  
*cis*

*cis*  
*cis*

*v*: measured visually

*d*: measured by diffractometer

*a*: partial double bond

*b*: double bond

*c*: C—OH bond

*e*: C=O bond



Table 7. Comparison of bond angles found in various pseudoguaianolide derivatives

	11,13-Dibromopulchellin		3-Bromoanhydrodehydrodihydropulchellin		Bromohelenalin	Bromo-mexicanin-E
	I	II	I	II		
C(2)—C(1)—C(5)	98°	101°	106°	102°	105°	108°
C(2)—C(1)—C(10)	119	118	113	116	115	114
C(5)—C(1)—C(10)	118	118	120	122	117	117
C(3)—C(2)—C(1)	109	106	102	106	111	108
C(3)—C(2)—O(2)	114	113	128	128		
C(1)—C(2)—O(2)	108	109	130	125		
C(4)—C(3)—C(2)	110	105	115	116	114	114
C(4)—C(3)—Br			125	125	121	118
C(2)—C(3)—Br			120	120	125	128
C(5)—C(4)—C(3)	99	110	110	108	105	107
C(5)—C(4)—O(4)	103	111			125	124
C(3)—C(4)—O(4)	116	109			130	129
C(6)—C(5)—C(1)	119	116	118	115	111	115
C(6)—C(5)—C(4)	110	116	109	107	110	109
C(6)—C(5)—C(15)	109	107	108	107	114	
C(1)—C(5)—C(4)	103	100	103	106	103	102
C(1)—C(5)—C(15)	118	109	109	112	115	
C(4)—C(5)—C(15)	95	108	110	109	104	
C(7)—C(6)—C(5)	112	116	113	114	116	113
C(7)—C(6)—O(6)					106	
C(5)—C(6)—O(6)					108	
C(8)—C(7)—C(6)	107	121	112	113	121	118
C(8)—C(7)—C(11)	103	105	101	103	102	102
C(6)—C(7)—C(11)	114	113	115	113	119	105
C(9)—C(8)—C(7)	113	120	113	118	120	121
C(9)—C(8)—O(8)	102	119	107	110	105	108
C(7)—C(8)—O(8)	99	98	106	103	101	105
C(10)—C(9)—C(8)	104	116	112	110	115	117

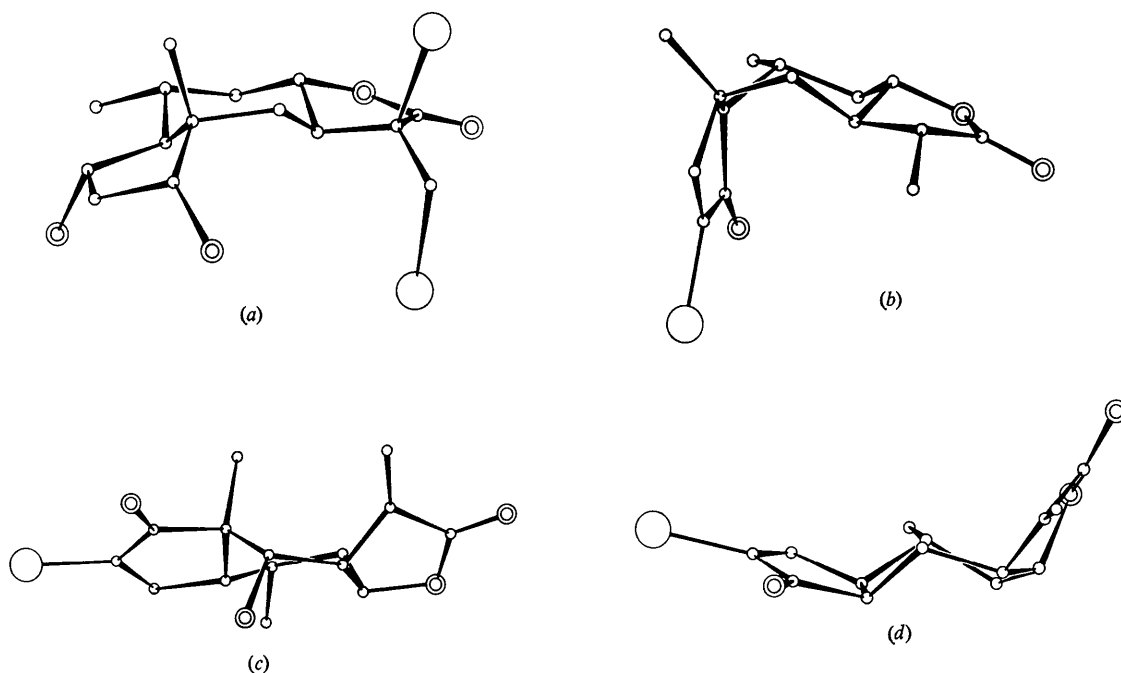


Fig. 5. Perspective drawing of the molecules found in various pseudoguaianolide derivatives showing the conformation of the molecule. Bromine atoms are indicated by large circles, oxygen by double circles and carbon by small circles. (a) 11,13-Dibromopulchellin, molecule II, viewed along  $[10\ 1\ 20]$ . Absolute configuration as determined by the X-ray method. (b) 3-Bromoanhydrodehydrodihydropulchellin, molecule I, viewed along  $[9\ 10\ 1]$ . (c) Bromohelenalin viewed along  $[20\ 7\ 1]$ . (d) Bromomexicanin-E viewed along  $[20\ 12\ 9]$ . This figure shows the methyl group attached to C(10) as being *cis* to C(1)- $\alpha$ H in contradiction to the chemical structure shown in the original paper (Mazhar-Ul-Haque & Caughlan, 1967) but in accordance with the atomic coordinates given in the same paper.

Table 7 (cont.)

	I	II	I	II		
C(14)–C(10)–C(1)	115	110	111	108	109	110
C(14)–C(10)–C(9)	99	105	109	111	113	110
C(1)–C(10)–C(9)	112	112	115	116	111	109
C(12)–C(11)–Br(11)	101	104				
C(12)–C(11)–C(7)	103	99	96	99	102	106
C(12)–C(11)–C(13)	121	117	119	113	123	121
Br(11)–C(11)–C(7)	114	112				
Br(11)–C(11)–C(13)	97	106				
C(7)–C(11)–C(13)	120	119	115	115	135	134
O(8)–C(12)–C(11)	108	110	114	113	110	109
O(8)–C(12)–O(12)	129	126	127	119	123	124
C(11)–C(12)–O(12)	122	124	119	127	127	126
C(8)–O(8)–C(12)	114	121	109	108	110	111
Br(13)–C(13)–C(11)	98	116				
Standard deviation	2.3–3.2	2.3–3.3	0.9–1.7		0.6–0.9	1.07–1.48

proposed by Aota *et al.* (1970) on the basis of stereochemical correlations with other pseudoguaianolides, aromaticin, mexicanin I and isotenulin. However, the *absolute* configuration in their case contains some uncertainty because their result was based on an assumption of the *absolute* configuration of bromoisotenulin (Rogers & Mazhar-Ul-Haque, 1963) which was derived only from optical rotatory dispersion evidence (Herz, Romo de Viver, Romo & Viswanathan, 1963).

Pulchellidine is derived by adding piperidine to pulchellin (Yanagita *et al.*, 1969). This reaction at the atom C(13) is stereospecific as in the bromination reaction by which the present compound, 11,13-dibromopulchellin, is derived. It is, therefore, reasonable to conclude that the C(11)–CH<sub>2</sub>NC<sub>3</sub>H<sub>10</sub> side chain in pulchellidine is directed *cis* with respect to C(7)– $\alpha$ H. The absolute stereostructures of pulchellin and pulchellidine are shown in Fig. 1(a) and (b).

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