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A Novel Pseudotwistane, Pulchellon from *Gaillardia pulchella*[*,1,2]

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A novel pseudotwistane named pulchellon was first isolated from a collection of *Gaillardia pulchella* as a minor constituent along with the pseudoguianolide alkaloids, pulchellidine and neopulchellidine. The absolute stereostructure of pulchellon (I) as designated in Fig. 6 has been completely established on the basis of its chemical and spectral evidences together with the biogenetic consideration as well as the direct X-ray crystallographic analysis of pulchellon. A possible biogenetic pathway of I through the keto key intermediate (VII) derived from another constituent pulchellin (III) has also been proposed.

It has recently been reported from our laboratory that new type of sesquiterpene alkaloids, pulchellidine[4] and neopulchellidine[5] were isolated from a collection of the title plant grown near St. Augustin Florida with a new minor constituent referring to Compound H.[4a] The present paper concerns the structural elucidation of Compound H, now named pulchellon, which possesses a unique pseudotwistane[6] skeleton as shown by formula (I) (Fig. 6). This contribution involves the first presentation of the natural occurrence of the pseudotwistane, the structural elucidation and a proposal of its biogenetic scheme.

Pulchellon (I), mp 225—227°, $[\alpha]_D$ $-66°$, $C_{12}H_{18}O_3$ was found to possess one tertiary and one secondary methyl group by observation of a singlet at 0.89 ppm and a doublet at 1.06 ppm (J=6 Hz), respectively, in the proton nuclear magnetic resonance spectrum (^{1}H-NMR). A broad singlet at 4.70 ppm attributable to two hydroxyl protons in I disappeared on addition of deuterium hydroxide. Acetylation of I with acetic anhydride and pyridine at room temperature gave the corresponding diacetate (II), mp 98—100°, $[\alpha]_D$ $-60°$, $C_{16}H_{22}O_5$, whose infrared spectrum (IR) exhibited two acetoxy absorptions at 1748 and 1738 cm^{-1} in place of hydroxyl absorptions at 3454 and 3357 cm^{-1} of I. ^{1}H-NMR spectrum of II further indicated the presence of the tertiary methyl (1.06 ppm), and secondary methyl (1.16 ppm, J=6 Hz) as well as two

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* Dedicated to the Memory of Prof. Eiji Ochiai.

1) This article is gratefully dedicated to late Dr. Eiji Ochiai for his invaluable encouragement and stimulating influence on the author's own research.

2) Presented at the 17th Symposium on the Chemistry of Natural Products of Japan, Tokyo, Oct., 17—19, 1973, Symp. Papers p. 49, and at the 18th Symposium of Perfume, Terpene and Ethereal Oil, Chiba, Sep. 28—30, 1974, Papers Abstracts p. 198.

3) Location: *a) 35 Shinanomachi, Shinjuku-ku, Tokyo*; *b) 3-1 Hongo-7-Chome, Bunkyo-ku, Tokyo.*

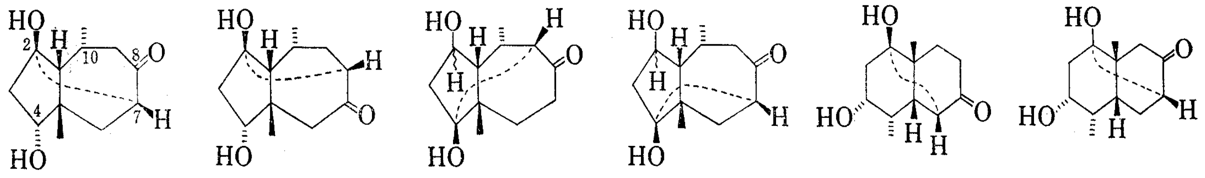
4) *a*) M. Yanagita, S. Inayama, T. Kawamata, T. Ohkura, and W. Herz, *Tetrahedron Letters*, **1969**, 2073, 4170; *b*) M. Yanagita, S. Inayama, and T. Kawamata, *ibid.*, **1970**, 131; *c*) T. Kawamata and S. Inayama, *Chem. Pharm. Bull.* (Tokyo), **19**, 643 (1971); *d*) T. Sekita, S. Inayama, and Y. Iitaka, *Tetrahedron Letters*, **1970**, 135; *idem*, *Acta Crystallogr.*, **B27**, 877 (1971).

5) M. Yanagita, S. Inayama, and T. Kawamata, *Tetrahedron Letters*, **1970**, 3007.

6) The first proposition of the use of a convenient trivial or a short pet name "pseudotwistane" has been made here for compounds which constitute any tricyclo[5.3.0.0]decane skeleton. The carbon framework of this dissymetric tricyclodecane derivatives differs from those of its isomers, which are composed of all cyclohexane rings, such as twistane [H.W. Whitlock, Jr., *J. Am. Chem. Soc.*, **84**, 3412 (1962)] *i.e.* tricyclo-[4.4.0.0^{3,8}]decane or adamantane [M. Nomura, P. von R. Schleyer and A.A. Arz, *ibid.*, **89**, 3657 (1967) and earlier references] *i.e.* tricyclo[3.3.1.1^{3,7}]decane.

acetoxy groups (1.98 and 2.08 ppm). The secondary hydroxyl group in I was assigned by downward shift of the methine proton appeared at 3.70 ppm to 4.85 ppm on acetylation even if measured in a different solvent, and none of the hydroxyl proton was observed in II. All the above spectral data for I and II support the presence of a normal secondary and a tertiary hydroxyl group which is readily acetylated. The absorption band at about 1710 cm^{-1} in the IR and the maximum at about 285 nm in the ultraviolet (UV) spectrum of I and II revealed the presence of the saturated carbonyl group in a six-membered or a larger ring system, which was further evidenced by formation of the yellow 2,4-dinitrophenylhydrazone. On the other hand, the Raman spectrum of II exhibited no band around 1600—1700 cm^{-1} to be assigned to a double bond as same as in the IR spectra of I and II. The absence of a double bond was supported not only by the negative tetranitromethane color test for I and II, but by the absence of the protons and carbon signals ascribable to the double bond in the ^{1}H- and ^{13}C-NMR spectra of I. Therefore, the empirical formula for pulchellon should have a tricyclic carbon skeleton, on which a bridgehead tertiary, a secondary hydroxyl group and one ketone function must be located. In addition, the negative periodic acid test for I suggests that the two hydroxyl groups do not adjoin each other, and the positive Zimmerman test for 1 and II reveals that pulchellon contains at least one active methylene group neighboring to the keto carbonyl.

As seen in the ^{1}H-NMR spectrum of II, the signal of the proton attached to the carbon atom bearing secondary acetoxy group is observed at 4.85 ppm as an octet with coupling constants $J=10$ Hz (3-H/4-H), 5 Hz (3′-H/4-H) and 2.5 Hz (4-H/6-H),[7] and the methine proton neighboring to the ketone appears at 3.05 ppm as a doublet of double doublets with coupling constants $J=9$ Hz (6-H/7-H), 2 Hz (6′-H/7-H) and 2 Hz (7-H/9-H). Comparing these observed J-values with the theoretical ones calculated from dihedral angles for the possible structures A, B, C, D, E and F as shown Fig. 1, the structures D. E and F should be apparantly eliminated on the basis of each widely different calculated J-values from the corresponding observed ones. Both the coupling constants calculated of the keto methine proton in the tricyclo-[5.3.0.0^{4,9}]decane structure C ($J=0$, 2, 2 or 0, 2, 2) and those in the tricyclo[5,3,0.0^{2,8}]decane structure B ($J=7.5$, 2, 0) are never consistent with the respective observed ones ($J=9$, 2, 2), while the values calculated of the acetoxy methine proton for B ($J=9$, 6, 2) and those for C ($J=10$, 4, 4 or 10, 4, 1) happen to coincide with the corresponding observed ones ($J=10$, 5, 2.5). However, there is no descrepancy in the tricyclo[5.3.0.0^{2,7}]decane structure A between the calculated values ($J=9$, 6, 2 and $J=10$, 4, 2) and the observed ones. The result of ^{1}H-NMR spin decoupling experiments is also in favor of the structure A: When irradiated at the highest frequency of the methylene region around 1—1.4 ppm in II, an octet signal due to C(4) methine proton with coupling constants of 10, 5 and 2.5 Hz changed to a doublet of doublet with those of 10 and 5 Hz. That is, the long range coupling ($J=2.5$ Hz) between the above C(4) methine proton and one of the methylene protons at C(6) has been collapsed. No such a spin coupling could be observed at all between the questioned methine proton at C(4) and one of the alternative methylene protons at C(9) in the structure B. Hence, it is



A B C D E F

Fig. 1. Possible Structures of Pulchellon (I)

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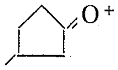
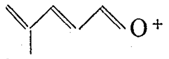
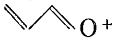
[7] The J-values calculated from the endocyclic torsion angle of C(6) and C(7) ($-6.9°$) in Fig. 5 mentioned below have been found to be 9.8, 2.5 and 2.5 Hz.

Table I. *J*-Values of Methine Protons which are neighbored to the Ketone and attached to the Acetoxy Group

Target proton	$\overset{\text{H}}{\overset{\vert}{>\text{C}}}\text{–OAc}$	$\overset{\text{O}}{\overset{\Vert}{\text{–C}}}\text{–}\overset{\text{H}}{\overset{\vert}{\text{C}}}\text{<}$
J-Value / Structure	Observed	
	10, 5, 2.5	9, 2, 2
	calculated	
A (4βH)	9, 6, 2	10, 4, 2
B (4βH)	9, 6, 2	7.5, 2, 2
C (2βH)	10, 4, 4	0, 2, 2
(2αH)	10, 4, 1	0, 2, 2

Table II. Mass Fragmentation of Diacetylpulchellon (II)

$C_{16}H_{22}O_5$	294	M^+
$C_{14}H_{20}O_4$	252	M^+–C_2H_2O
$C_{14}H_{18}O_3$	234	M^+–HOAc
$C_{12}H_{18}O_3$	210	M^+–2 × C_2H_2O
$C_{12}H_{16}O_2$	192	M^+–C_2H_2O–HOAc
$C_6H_{10}O$	98	
C_6H_7O	95	
C_4H_5O	69	
C_3H_3O	55	

obvious that the structure A can only satisfy the observed *J*-value discussed above (Table I). The ^{13}C–NMR spectrum of I and the mass fragmentation of II (Table II) are also in good coincidence with the structure A of pulchellon (I). The above mentioned facts finally allow us to accomodate only one pseudotwistane expression A among several possibilities *e.g.* A, B, C, D, E and F for the structure of pulchellon.

Concerning the stereochemistry of pulchellon, if C(5)–CH_3 was tentatively assumed to be β-oriented[8] regarding pulchellin (III)[4,9] as a biogenetic precursor of pulchellon (I) as discussed below, the configuration of C(1)–H should be represented by β. The steric situation of C(1)–H and C(5)–Me must be in *cis* relationship in order to form the C(2)–C(7) bond, which necessitates C(2)–OH to take the β-orientation. The α configuration of C(4)–OH, on the other hand, is deduced from the NMR coupling constants of the C(4)–H as shown in Table I. The configuration of C(10)–Me seems to be α providing that the biogenetic consideration as above would be acceptable. The most probable structure of I is now formulated by 2β,4α-dihydroxy-5β,10α-dimethyltricyclo[5.3.0.0^{2,7}]decane-8-one being composed of a cycloheptane, two cyclopentanes and two cyclohexanes which are all twisted.

The optical rotatory dispersion (ORD) and circular dichroism (CD) curves of I display relatively weak negative Cotton effects in methanol solution at 276—308 nm and 292 nm, respectively (Fig. 2), which are in accord with those predicted from the octant sector diagram (A) of the conformer A of pulchellon (Fig. 3). The cyclohexane ring attached to the norbornane moiety takes the chair form in the conformer A, whereas it does the boat form in the

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[8] The angular methyl group of pseudoguaianoids isolated so far from Gaillardia and its related genera of Compositae used to possess the β-configuration. It has been found to be the case in I on the basis of its X-ray crystallographic analysis described later.

[9] *a*) W. Herz, K. Ueda, and S. Inayama, *Tetrahedron*, **19**, 483 (1963); *b*) K. Aota, C.N. Caughlan, M.T. Emerson, W. Herz, S. Inayama, and Mazhar-Ul-Haque, *J. Org. Chem.*, **35**, 1448 (1970).

comformer B. Consequently, pulchellon should favor the conformation A in solution if the octant sector rule[10] was applicable to the present pseudotwistane system. Further proof on the conformation of pulchellon has been lastly provided by its X-ray analysis described later, which reveals a half chair conformation of the cyclohaxane ring attached to the norbornane moiety of the molecule. It can be conceivable that pulchellon might take a mobile conformation of the cyclohaxane ring in solution accompanying an equilibration between the chair form of the conformer A and the distorted half chair form in the crystal.

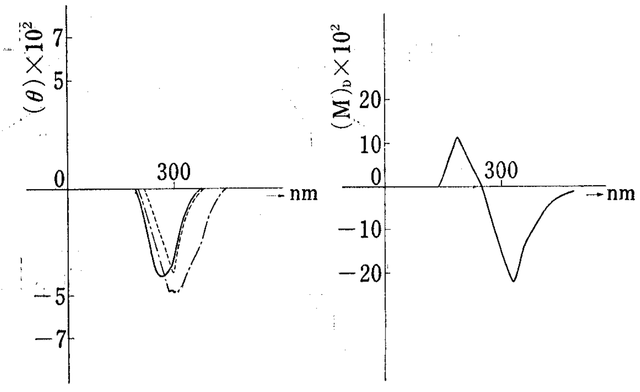
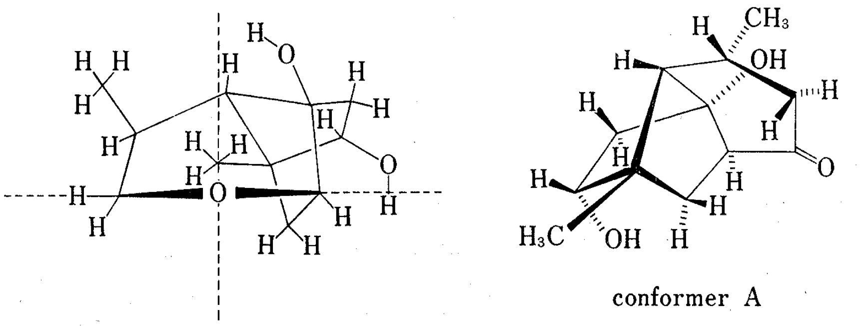
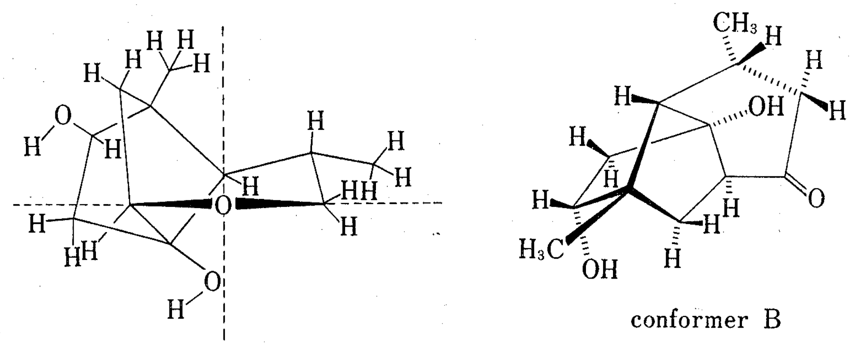


Fig. 2. ORD and CD Curves of Pulchellon (I)

— MeOH, ··· $CHCl_3$, —·— dioxane



conformer A



conformer B

Fig. 3. Octant Sector Diagrams and Conformations of Pulchellon (I)

In connection with the above argument in favor of the stereochemistry of pulchellon, it is of significance to add some discussion on a possible biogenetic pathway from pulchellin (III)[4,9] to pulchellon (I) as described below (Chart 1).[2] Incidentally, the similar assumption on biogenesis of III has already been proposed for all the other sesquiterpenolides obtained from the same plant.[11] First, an intermediate α-ketol (V)[9a] would probably form from III *via* norpulchellone (IV) by an oxidative cleavage of the lactone ring. Subsequently, either the isomeric ketol (V)′ or the epoxide (VI) derived from V would lead to the keto key inter-

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10) W. Moffitt, R.B. Woodward, A. Moscowitz, W. Klyne, and C. Djerassi, *J. Am. Chem. Soc.*, **83**, 4013 (1961); C. Djerassi and W. Klyne, *Proc. Nat. Acad. Sci. U.S.*, **48**, 1093 (1962).

11) S. Inayama, T. Kawamata, and M. Yanagita, *Phytochemistry*, **12**, 1741 (1973).

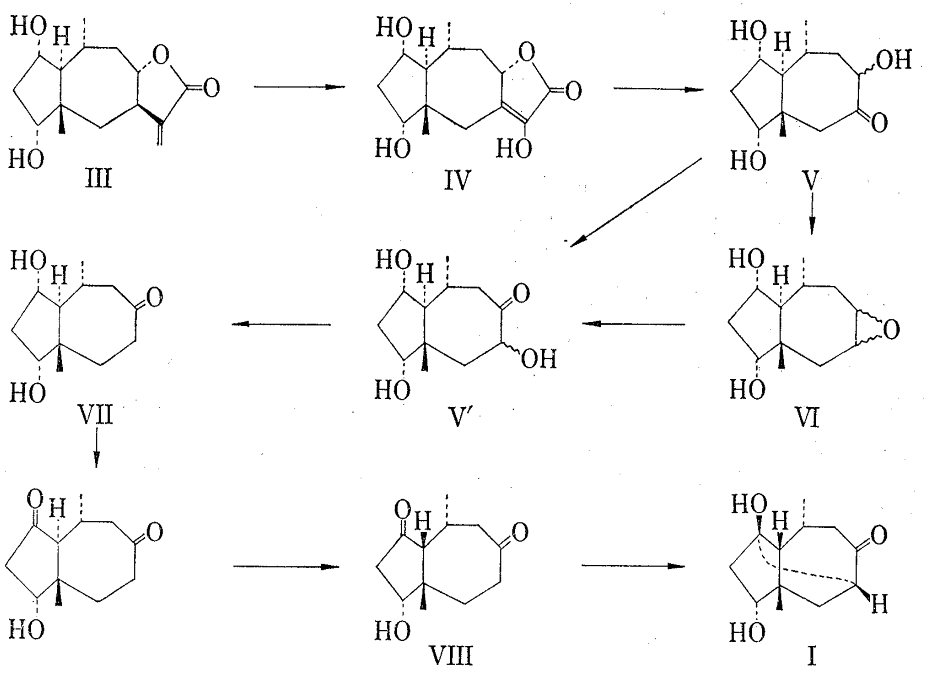

Chart 1. A Possible Biogenetic Pathway of Pulchellon (I) from Pulchellin (III)

mediate (VII).[12] The selective oxidation of C(2)–OH in VII followed by epimerization of C(1)–H at the ring juncture would furnish *cis*-4α-hydroxy-5β,10α-dimethylbicyclo[5.3.0]decane-2, 8-dione (VIII). The final transannular cyclization between C(2) and C(7) would result in formation of 2β,4α-dihydroxy-5β,10α-dimethyltricyclo[5.3.0.$0^{2,7}$]decan-8-one, *i.e.* pulchellon (I). An attempt at the chemical transformation of III to I, the former of which possess the established absolute configuration as shown in Chart 1,[4a,cf.9b] is now in progress through the possible biogenetic pathway mentioned above. It must be, however, clarified by any means in advance of such a biomimetic transformation whether pulchellon definitely has the right absolute configuration as was expected. This was really solved by a three dimentional X-ray structure analysis of pulchellon itself.

The lattice parameters and intensity data were derived from the measurements on a Phillips four-circle X-ray diffractometer with monochromatic Cu$k\alpha$ radiation. The intensity data were collected by the θ–2θ scan method up to $2\theta=156°$ with the scan speed of $\theta=4°/\text{min}$. The background was counted at each end of the scan for half the scan time. The crystal data so obtained are as follows: $C_{12}H_{18}O_3$, mol. wt.$=$210.126. Orthorhombic, $a=11.167$ (8), $b=11.724$ (8), $c=8.301$ (5) Å, $U=1086.8$ Å^3, $Z=4$, $Dx=1.288$ g/cm^3 and space group $P2_12_12_1$. The net intensity data were corrected for Lorentz and polarization factors but not for absorption factors. A total of 1264 non-zero independent reflections were observed out of 1299 theoretically possible ones. The structure was solved by the direct method and was refined by several cycles of block-diagonal least-squares calculations. R-factor was 0.094 at this stage for non-hydrogen atoms. Further refinement was carried out including all the hydrogen atoms found on the difference electron-density map. The final R-factor was 0.067 assuming anisotropic thermal motions for non-hydrogen atoms and isotropic ones for hydrogen atoms. The unit weight was assigned for each reflection during the least-squares calculations. The used atomic scattering factors for C and O atoms were those given in International Tables for X-ray Crystallography Vol. III[13] and for H were those given by Stewart, Davidson and

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12) Unpublished data in our laboratory.
13) International Tables for X-ray Crystallography, Vol. III. Kynoch Press, Birmingham (1962).

Table III. Fractional Atomic Coordinates and Temperature Factors

	x	y	z	$\beta 11$	$\beta 22$	$\beta 33$	$\beta 12$	$\beta 13$	$\beta 23$
O 1	6830(3)	3375(3)	4971(5)	40(3)	35(3)	87(6)	6(3)	30(4)	7(4)
O 2	8968(4)	4390(3)	191(5)	66(4)	35(3)	61(6)	9(3)	16(4)	15(4)
O 3	9749(5)	3652(5)	7178(5)	78(4)	90(5)	53(7)	−11(4)	−1(5)	−19(5)
C 1	8134(5)	2201(4)	3183(7)	39(4)	21(3)	68(8)	−1(3)	6(5)	2(5)
C 2	7772(5)	3388(4)	3823(7)	30(4)	25(3)	60(8)	1(3)	12(5)	4(5)
C 3	7477(5)	4057(5)	2282(7)	45(4)	39(4)	70(9)	19(4)	12(6)	10(5)
C 4	8302(5)	3517(5)	1005(7)	49(5)	35(4)	61(8)	5(4)	9(6)	9(5)
C 5	9104(5)	2693(4)	2013(7)	40(4)	24(3)	52(8)	5(3)	5(5)	−3(5)
C 6	9887(5)	3420(5)	3162(7)	33(4)	39(4)	50(8)	−4(4)	8(5)	0(5)
C 7	8986(5)	3816(5)	4504(7)	41(4)	33(4)	55(8)	−4(4)	7(5)	−6(5)
C 8	9266(5)	3187(6)	6050(7)	42(4)	57(5)	60(9)	4(4)	15(6)	−3(6)
C 9	8853(6)	1940(6)	6126(8)	68(6)	51(5)	64(9)	0(5)	−1(6)	21(6)
C 10	8648(5)	1367(5)	4463(7)	51(5)	28(4)	76(9)	3(4)	14(6)	13(5)
C 11	7826(7)	327(5)	4681(9)	88(7)	32(4)	144(13)	−13(5)	18(9)	21(7)
C 12	9833(6)	1868(5)	993(8)	73(6)	39(4)	92(10)	22(4)	26(7)	−10(6)
C 1H	720(6)	185(6)	246(8)	35(16)					
C 3HA	655(6)	399(5)	193(8)	24(15)					
C 3HB	773(5)	496(5)	242(7)	11(12)					
C 4H	734(7)	308(7)	16(11)	67(22)					
C 6HA	1035(5)	415(5)	255(8)	22(14)					
C 6HB	1075(5)	292(5)	352(7)	23(14)					
C 7H	895(6)	486(6)	462(9)	38(17)					
C 9HA	956(8)	140(8)	680(10)	70(25)					
C 9HB	793(7)	189(7)	680(10)	59(22)					
C 10H	967(8)	80(7)	408(10)	71(23)					
C 11HA	779(5)	−11(5)	369(8)	21(14)					
C 11HB	690(6)	53(5)	514(8)	25(14)					
C 11HC	803(7)	−15(7)	528(11)	66(23)					
C 12HA	1058(7)	143(7)	149(10)	52(21)					
C 12HB	1061(5)	235(5)	25(8)	27(14)					
C 12HC	955(7)	142(6)	50(9)	48(20)					
O 1H	666(6)	393(6)	506(9)	37(18)					
O 2H	921(5)	431(5)	−29(8)	21(14)					

Standard deviations are given in parentheses denoting the least significant digits. x, y and z values are multiplied by 10^4 for non-hydrogen atoms and by 10^3 for hydrogen atoms. Temperature factors for non-hydrogen atoms are of the form, $T=\exp\{(-\beta_{11}h^2+\beta_{22}k^2+\beta_{33}l^2+2\beta_{12}hk+2\beta_{13}hl+2\beta_{23}kl)\}$ where β_{ij} values are multiplied by 10^4. Those for hydrogen atoms are of the form, $T=\exp\{-\beta_{11}(\sin\theta/\lambda)^2\}$ where β_{11} values are multiplied by 10.

Simpson.[14] The final atomic parameters are given in Table III with their standard deviations and the observed and calculated structure factors are listed in Table IV.

The absolute configuration was determined using the anomalous dispersion effect of the oxygen atoms. The $\Delta f'$ and $\Delta f''$ values for Cukα radiation were adopted to be 0.0 and 0.1, respectively.[13] The intensity data for Friedel pairs were remeasured with considerable accuracy.[15] Comparison of the observed and calculated $|F(hkl)|^2/|F(\bar{h}\bar{k}\bar{l})|^2$ values (Table V) established the absolute configuration as shown in Fig. 4. Bond lengths and angles not including hydrogen atoms are shown in Fig. 4. The average standard deviations estimated for C–C bond lengths and C–C–C angles are 0.008 Å and 0.5°, respectively. The angle C(2)–C(1)–C(5) is significantly smaller than the tetrahedral angle, since C(1) is situated at the bridge

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14) R.F. Stewart, E.R. Davidson, and W.T. Simpson, *J. Chem. Phys.*, 42, 3175 (1965).

15) The crystal of the size $0.2\times0.3\times0.5$ mm was used. The conditions of intensity measurement were the same as stated before but four measurements on hkl and $\bar{h}\bar{k}l$, $\bar{h}kl$, $h\bar{k}l$ reflections were made for each hkl reflection and the two averages for hkl and $\bar{h}\bar{k}l$, and $\bar{h}kl$ and $h\bar{k}l$ were taken to represent $|\text{Fobs}(hkl)|^2$ and $|\text{Fobs}(\bar{h}\bar{k}\bar{l})|^2$, respectively.

Table IV. Observed and Calculated Structure Factors

K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC	K	FO	FC
H,L=	0	0	7	4	5	11	5	5	1	3	3	4	3	1	13	5	5	H,L=	10	3	8	9	9	3	16	14	H,L=	12	5	8	3	3	5	7	7
2	61	69	9	2	3	12	14	15	2	6	6	5	18	16	14	5	6	1	2	2	9	9	9	4	7	6	0	4	4	H,L=	9	6	H,L=	10	7
4	67	71	10	3	4	13	6	6	3	2	2	6	7	7	H,L=	2	3	2	8	9	10	3	3	5	17	17	1	5	5	2	10	10	1	1	1
6	46	44	12	1	1	14	6	7	4	3	3	7	10	10	0	37	35	3	7	7	11	3	3	6	5	5	2	7	8	3	5	5	2	7	7
8	9	8	H,L=	9	0	H,L=	4	1	5	2	2	8	11	10	1	26	24	4	6	6	12	6	6	7	10	10	3	2	2	4	7	8	3	5	6
10	18	17	1	4	4	0	15	12	6	7	8	9	6	6	2	7	5	5	3	3	H,L=	6	4	8	15	16	H,L=	0	6	5	6	6	H,L=	0	8
12	1	2	2	13	12	1	19	17	7	2	2	10	7	7	3	35	33	6	4	4	0	4	4	9	4	4	0	1	2	6	3	3	0	5	5
14	3	3	3	12	11	2	24	22	H,L=	13	1	11	9	9	4	38	36	7	3	3	1	12	12	10	2	2	1	21	20	7	1	1	1	3	4
H,L=	1	0	4	2	1	3	22	20	0	3	3	12	9	9	5	17	16	8	4	4	2	12	12	11	1	0	2	3	3	H,L=	10	6	2	3	3
1	45	49	5	9	7	4	34	32	1	8	9	13	7	8	6	14	13	9	3	3	3	10	9	12	4	5	3	9	9	0	11	11	3	12	13
2	47	48	6	4	5	5	23	22	2	4	4	H,L=	7	2	7	11	11	H,L=	11	3	4	4	5	H,L=	3	5	4	13	13	1	2	2	4	3	3
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6	14	12	10	3	3	9	15	16	H,L=	14	1	4	18	18	11	6	5	3	5	6	8	2	2	3	11	9	8	3	4	5	10	11	8	15	16
7	16	14	11	1	2	10	8	9	0	1	0	5	11	9	12	5	6	4	3	4	9	4	4	4	12	12	9	3	2	6	2	3	H,L=	1	8
8	7	6	H,L=	10	0	11	16	16	1	2	2	6	13	14	13	3	4	6	3	3	10	1	1	5	7	6	10	9	9	H,L=	11	6	0	16	17
9	18	17	0	20	21	12	5	6	H,L=	0	2	7	4	4	14	3	4	7	3	3	11	10	11	6	11	11	11	7	7	0	1	1	1	21	21
10	2	2	1	11	11	13	3	3	0	43	44	8	6	7	H,L=	3	3	8	4	5	12	7	7	7	4	4	12	1	0	1	5	5	2	6	6
11	8	8	2	8	8	14	6	7	1	12	13	9	4	3	0	6	5	H,L=	12	3	H,L=	7	4	8	5	5	H,L=	1	6	2	4	4	3	10	11
12	12	13	3	11	11	H,L=	5	1	2	38	38	10	5	5	1	6	7	0	9	9	0	17	17	9	4	4	0	5	5	3	6	5	4	7	8
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14	3	3	5	15	14	1	5	5	4	12	9	12	2	2	3	41	37	2	3	3	2	15	15	11	6	7	2	5	4	H,L=	0	7	6	3	3
H,L=	2	0	9	3	3	2	27	23	5	13	12	H,L=	8	2	4	19	16	3	2	2	3	12	11	12	5	6	3	2	2	1	4	5	7	4	4
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4	18	16	H,L=	11	0	7	17	16	10	14	14	4	12	11	9	12	12	1	1	1	8	10	9	3	3	3	8	3	3	7	4	5	2	2	2
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7	3	3	3	2	4	10	3	2	13	6	7	7	7	7	12	4	5	4	3	4	11	2	2	6	14	13	11	5	6	0	23	24	5	4	4
8	2	2	4	7	8	11	2	2	14	3	3	8	5	5	13	5	5	H,L=	0	4	H,L=	8	4	7	8	9	12	8	9	1	15	15	6	9	10
9	8	7	5	8	9	12	5	5	H,L=	1	2	9	3	3	H,L=	4	3	0	29	29	0	3	1	8	9	9	H,L=	2	6	2	11	11	7	10	10
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H,L=	3	0	H,L=	12	0	2	22	19	4	41	39	1	20	21	4	11	9	5	1	0	5	10	11	H,L=	5	5	4	6	5	7	3	4	2	16	16
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5	20	19	9	16	16	H,L=	12	1	2	11	10	11	7	6	9	7	7	6	10	9	1	4	4	5	5	5	6	11	11	2	2	3			
6	6	6	10	12	11	0	9	11	3	15	14	12	6	6	10	5	6	7	11	11	2	9	8	6	2	3	7	2	1	3	3	3			

Table V. Comparison of Observed and Calculated Intensity Ratios Between a Pair of Friedel Reflections used for the Establishment of Absolute Configuration

h	k	l	$\frac{\lvert F_{obs}(hkl)\rvert^2}{\lvert F_{obs}(\bar{h}\bar{k}\bar{l})\rvert^2}$	$\frac{\lvert F_{cal}(hkl)\rvert^2}{\lvert F_{cal}(\bar{h}\bar{k}\bar{l})\rvert^2}$	h	k	l	$\frac{\lvert F_{obs}(hkl)\rvert^2}{\lvert F_{obs}(\bar{h}\bar{k}\bar{l})\rvert^2}$	$\frac{\lvert F_{cal}(hkl)\rvert^2}{\lvert F_{cal}(\bar{h}\bar{k}\bar{l})\rvert^2}$
1	8	1	0.96(2)	1.16	4	10	2	0.94(2)	1.12
4	12	1	0.90(3)	1.05	2	10	3	1.05(2)	0.89
5	5	1	1.05(1)	0.93	5	5	3	1.05(2)	0.93
10	1	1	1.08(3)	0.93	3	3	4	0.92(3)	1.09
11	5	1	0.91(3)	1.14	4	6	4	1.06(1)	0.93
2	5	2	0.93(1)	1.20	1	2	5	0.95(2)	1.11
3	4	2	1.05(1)	0.92	2	4	5	1.13(2)	0.93
3	9	2	0.82(5)	1.13					

E.s.d.'s of observed ratios are given in parentheses denoting the least significant digit.

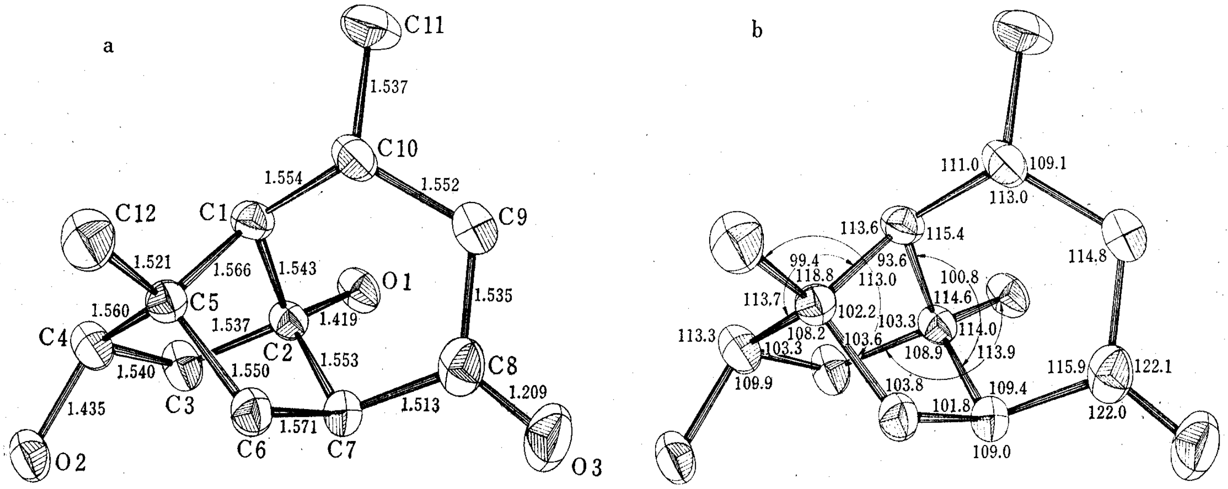

Fig. 4. Perspective Drawings Showing the Conformation and the Absolute Configuration of the Molecule

The ellipsoid represents the thermal vibrations of atoms enclosing the region where the centre of the atom will find with probability greater than 50%. Bond lengths and angles are given in (a) and (b), respectively.

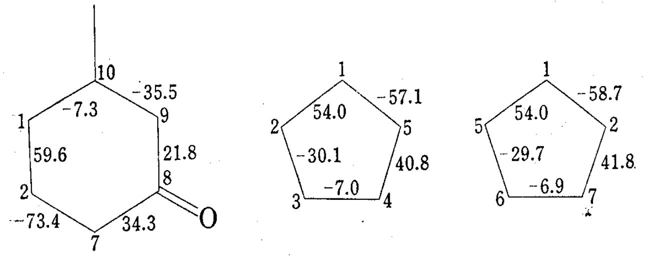

Fig. 5. Endocyclic Torsion Angles Given for Each Ring which show the Conformation of the Ring

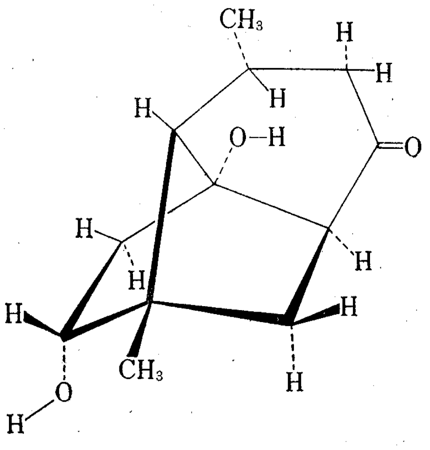

Fig. 6. The Stereostructure of Pulchellon (I)

head of the six-membered ring formed by C(2), C(3), C(4), C(5), C(6) and C(7) as found in the usual norbornane system. The conformation of each ring is shown in Fig. 5 by the endocyclic torsion angles. The two five-membered rings A and B take an envelope type while the conformation of the six-membered C ring is a distorted half chair.

In conclusion, the absolute structure of the molecule of pulchellon (I) has been established. It reveals that the conformation of the cyclohexane ring attached to the norbornane moiety is in a distorted half chair form as shown in Fig. 6. The stereochemical relationship in the complete structure of pulchellon, (−)-2β,4α-dihydroxy-5β,10α-dimethyltricyclo[5.3.0.0^{2,7}]-decan-8-one, is as follows: C(5)-β-CH_3/C(1)-β-H (*cis*-ring juncture); C(2)-β-OH/C(7)-β-H (*cis*-ring juncture); C(2)-β-OH/C(4)-α-OH (*trans*-1,3-diol); C(1)-β-H/C(10)-α-CH_3 (*trans*). The conclusion obtained from the X-ray analysis in a solid state is coincident with that deduced from the above mentioned spectral data in solutions and the biogenetic consideration as well, only except a slight difference in the conformation of the cyclohexane attached to the norbornane ring system. The synthetic approach to pulchellon is in progress to be reported in very near future.

Experimental

Melting points were determined on a Büchi's apparatus and are all uncorrected. The IR spectra were recorded on a Hitachi EPI-G3 instrument and the UV spectra were determined on a Shimazu double beam spectrophotometer UV-200. The proton and carbon NMR spectra were measured on a Varian A-60, a JEOL C-60H and a JNM MH-100 NMR spectrometer, and a JNM PS-100 carbon NMR spectrometer, respectively. Optical rotations, and ORD and CD spectra were run on a Jasco DIP-180 automatic polarimeter and Jasco ORD/UV-5 automatic spectrometer, respectively. The Mass spectra were measured on a JEOL MS-01SG high resolution mass spectrometer at 70 eV. The thin-layer chromatography (TLC) was performed on Silica gel G (Merck) plates with acetone/EtOH (1: 1). Gas chromatography (GLC) was conducted on a Hitachi KGL-2B (FID) gas chromatograph, using a glass column (2 m × 4 mm i.d.) with 1.5% OV-17 on Chromosorb W (80—100 mesh), column temperature 220°.

Isolation of Pulchellon (I)——The dried above-ground chipped material of *Gaillardia pulchella* collected near St. Augustin was extracted with hot chloroform in the usual manner. The crude gum weighing totally 189 g was taken up in a minimum amount of benzene/$CHCl_3$ (3: 1, 200 ml) and subjected to column chromatography over neutral alumina (2.5 kg). There was obtained a viscous oil (81.25 g) from the fraction eluted with benzene/$CHCl_3$ (9: 1) to the one eluted with benzene/$CHCl_3$ (3: 1), which, on treatment with ether, afforded the crude crystals, 28.62 g (15.14%), *Rf* 0.54 (major), 0.57 (minor) on TLC (silica gel, acetone/EtOH). Recrystallization from $CHCl_3$/ether, with combination of charcoal treatment and chromatography over neutral alumina, gave rise to a crystalline mixture of pulchellidine,[4)] colorless needles, mp 185—186° and neopulchellidine,[5)] fine needles, mp 131—134°.

The more polar fraction eluted with $CHCl_3$/MeOH (999: 1) and $CHCl_3$/MeOH (99: 1) on the same chromatography as above yielded an oil (6.32 g), which was crystallized from $CHCl_3$/ether to give rise to crude crystals weighing 0.437 g (0.023%), mp 215—225°. Several recrystallizations from MeOH/$CHCl_3$ furnished the analytical sample of pulchellon, mp 225—227°. $[\alpha]_D^{18}$ −66° (*c*, 1.0; EtOH). *Anal.* Calcd. for $C_{12}H_{18}O_3$: C, 68.54; H, 8.63. Found: C, 68.53; H, 8.44. Mass M^+ 210.123 (Calcd. 210.126). UV λ_{max}^{EtOH} nm (ε) 283.5 (25.5). IR ν_{max}^{KBr} cm^{-1} 3454, 3357 (O–H), 1700 (C=O). ^1H-NMR (DMSO-d_6) δ_{TMS} ppm 0.89 (3H, s, $\rangle C-C\underline{H}_3$), 1.05 (3H, d 6, $>CH-C\underline{H}_3$), 3.45 (1H, m, $>C\underline{H}-CO-$), 3.70 (1H, octet, 10, 5, 2.5, $>C\underline{H}-OH$), 4.70 (2H, brs, $>CH-O\underline{H}+\rangle C-O\underline{H}$) (disappeared on addition of D_2O). ^{13}C-NMR (CD_3OD) δ ppm (I^{rel}) 16.441 (355) (12-C), 24.935 (371) (11-C), 25.542 (319) (6-C), 29.910 (341) (10-C), 43.501 (329) (5-C), 44.593 (323) (1-C), [46.534 (276), 47.323 (558), 48.233 (1431), 49.082 (1502), 49.871 (1353), 50.781 (837), 51.570 (299)] (CD_3OD+3-C), 56.788 (371) (9-C), 58.790 (298) (7-C), 76.142 (369) (4-C), 83.665 (223) (2-C), 216.656 (230) (8-C). ORD (c=0.0583; MeOH) $[\alpha]^{23}$ (nm) −1066.6° (308) (trough), +566.6° (276) (peak) (a=−34.29). CD (c=0.0583; MeOH) $[\theta]^{23}$ (nm) −416.03 (292) (negative maximum). CD (c=0.0453; $CHCl_3$) $[\theta]^{23}$ (nm) −400 (297) (negative maximum). CD (c=0.0443; dioxane) $[\theta]^{23}$ (nm) −292 (311) (shoulder), −484 (302) (negative maximum), −473 (293) (hump). Yellow prisms of 2,4-dinitrophenylhydrazone (mp 210°) of I prepared in the usual manner exhibited UV absorbtion maxima at 231 and 365 nm.

Acetylation of I giving Diacetylpulchellon (II)——A sample of pulchellon (50 mg) was dissolved in pyridine (1 ml) and acetic anhydride (2 ml). The reaction mixture was allowed to stand overnight at room temperature. The residue remained after evaporation of solvent under reduced pressure was crystallized from EtOAc/ether to give prisms, mp 98—100°. $[\alpha]_D^{18}$ −60.0° (*c*, 0.3; EtOH). *Anal.* Calcd. for $C_{16}H_{22}O_5$: C, 65.29; H, 7.53. Found: C, 65.77; H, 7.54. Mass M^+ 294.147 (Calcd. 294.147). IR ν_{max}^{KBr} cm^{-1} 1748, 1738 ($OCOCH_3$), 1718 (C=O). UV λ_{max}^{EtOH} nm (ε) 285 (19.5). ^{1}H-NMR ($CDCl_3$) δ_{TMS} ppm 1.06 (3H, s, $>C{-}C\underline{H}_3$), 1.16 (3H, d 6, $>CH{-}C\underline{H}_3$), 1.98 (3H, s, $-OCOC\underline{H}_3$), 2.08 (3H, s, $-OCOC\underline{H}_3$), 3.05 (1H, ddd 9, 2, 2, $>C\underline{H}{-}CO{-}$), 4.85 (1H, ddd 10. 5, 2.5, $>C\underline{H}{-}OCOCH_3$).

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