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## The Structure of Conacytone, $C_{20}H_{26}O_6$ , a Diterpene Quinone from *Salvia ballotaeiflorae*\*

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Conacytone,  $C_{20}H_{26}O_6$ , is a diterpenoid quinone isolated from *Salvia ballotaeiflorae* Benth. The compound crystallizes in space group  $P2_12_12_1$  with cell dimensions  $a=13.620$  (3),  $b=12.666$  (3) and  $c=10.948$  (3) Å with  $Z=4$ . Counter techniques were used to collect 1759 independent reflections of which 1381 had intensities greater than  $3\sigma(I)$ . The structure was solved through application of the *MULTAN* direct methods program, and the model was refined by least-squares techniques to an  $R$  value of 0.047. The abietane type diterpene contains a bridging hemiacetal group. The  $A$  ring and the six-membered hemiacetal ring exhibit chair conformations while the  $B$  ring is a half-chair. The  $p$ -quinone ring deviates from planarity.

### Introduction

*Salvia ballotaeiflora* Benth was collected around Monterrey, Mexico, and ethereal extracts of the aerial parts yielded two quinones. Conacytone is a yellow crystalline solid with melting point of 240°C. The mass spectrum contains a small parent ion peak at 362 and an intense peak at 344 which is consistent with the loss of water. Chemical analyses and mass spectrometry established the molecular formula as  $C_{20}H_{26}O_6$ . (Found: C, 66.40; H, 7.31%. Calculated: C, 66.28; H, 7.23%). Icetexone is an orange crystalline quinone with a melting point of 248–250°C. Mass spectrometry and chemical analyses indicate the molecular formula to be  $C_{20}H_{22}O_5$ . We would like to report the crystal and molecular structure of conacytone.

### Experimental

A crystal of dimensions  $0.4 \times 0.4 \times 0.7$  mm was mounted with the  $c$  axis coincident with the rotation axis. The unit cell was found to be orthorhombic and room temperature cell dimensions were determined from calibrated precession and Weissenberg photographs. Crystal data are given in Table 1.

The intensity data,  $hk0$  through  $hk9$ , were collected with a Philips PAILRED diffractometer using equi-

Table 1. *Crystal data*

$C_{20}H_{26}O_6$ , M.W. 362.43,  $a=13.620$  (3),  $b=12.666$  (3) and  $c=10.948$  (3) Å,  $P2_12_12_1$  ( $D_2^4$ , No. 19),  $Z=4$ ,  $F(000)=776$ ,  $U=1889$  Å<sup>3</sup>,  $D_m=1.274$ ,  $D_c=1.274$  g cm<sup>-3</sup>,  $\mu=7.8$  cm<sup>-1</sup>.

inclination geometry and the continuous  $\omega$ -scan technique. A scan range of  $4.0$  to  $4.4^\circ$  at  $2.5^\circ$  min<sup>-1</sup> was used. A background count was taken for 20 s on either side of the  $\omega$ -scan range. Cu  $K\alpha$  radiation ( $\lambda=1.54178$  Å) and a graphite monochromator were used. A total of 1759 independent reflections was measured in the  $2\theta$  range less than  $140^\circ$ , and 1381 had intensities greater than  $3\sigma(I)$ . The intensities of the reference reflections did not change significantly during data collection. Lorentz and polarization corrections were applied, but no absorption correction was made. Structure factor magnitudes,  $|F_o|$ , and normalized structure factor magnitudes,  $|E_h|$ , were computed. The scattering factors of Cromer & Waber (1965) were used for the C and O atoms while those of Stewart, Davidson & Simpson (1965) were used for the H atoms.

### Structure determination and refinement

A *MULTAN* (Germain, Main & Woolfson, 1971) program package was used to calculate phases for the 302  $|E|$ 's greater than 1.3.  $E$  maps were generated for the two sets with the highest combined figures of merit. Reasonable molecular fragments were found in both maps; however, the map from the set with the second highest figure of merit exhibited a better distribution

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of peak intensities. The positions for a 24-atom model were selected and three cycles of block-diagonal least-squares refinement using C scattering factors yielded an  $R$  value of 0.35 where  $R = [\sum \Delta F_{\text{meas}} / \sum F_{\text{meas}}]$ . Six of the atoms were designated as O atoms, and five cycles of refinement reduced  $R$  to 0.236. The remaining atoms were found by recycling through *MULTAN* and from a difference Fourier map. Least-squares refinement of a 26-atom model reduced  $R$  to 0.171. Five low-angle reflections were removed from the set of 1381 intensities, and anisotropic least-squares refinement reduced  $R$  to 0.074. The positions of 23 H atoms were obtained from a difference map. Their contributions to the structure factors were calculated, but the parameters were not refined. Five cycles of least-squares refinement lowered  $R$  to 0.058. Before the final refinement, a peak search program was used to obtain accurate positional parameters for 25 H atoms from a difference Fourier map. The final least-squares refinement using 1376 reflections yielded  $R = 0.047$  and  $R_w = 0.060$  where  $R_w = [\sum w(\Delta F_{\text{meas}})^2 / \sum w F_{\text{meas}}^2]^{1/2}$ . The function minimized in the refinement was  $w(\Delta F_{\text{meas}})^2$  where  $w = [1/\sigma(F_o)]^2$ . Standard deviations were assigned on the basis of counting statistics (Stemple & Watson, 1972).

The final three-dimensional difference Fourier map showed no peak greater than about one half of that expected for a H atom. The H atom associated with O(26) could not be located. The estimated standard deviations were calculated from the inverse of the normal-equations matrix. All shifts of the parameters during the final cycle of refinement were less than one tenth of the estimated standard deviation. The atomic and thermal parameters along with the estimated stan-

dard deviations are given in Table 2. The thermal parameters contain a systematic error associated with the collection of data in the Weissenberg geometry with the Pailred system. While the absolute values are not reliable, the relative magnitudes are meaningful.\*

### Discussion

Fig. 1 shows the molecular structure of conacytone and gives the numbering system used in all Tables. Table 3 lists bond distances and bond angles while Table 4 lists torsion angles.

Conacytone, I, is an abietane type diterpene (Newman, 1972) and is related to the diterpene nemorone,

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31661 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1 NZ, England.

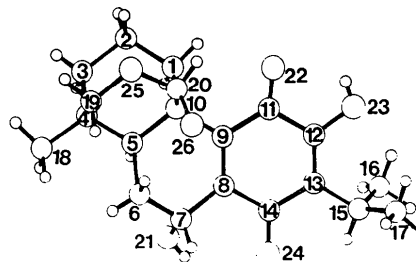


Fig. 1. Molecular structure of conacytone and the numbering scheme used in all tables.

Table 2. Atomic ( $\times 10^4$ ) and thermal ( $\times 10^3$ ) parameters

Anisotropic parameters have the form  $\exp [-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)]$ .

	$x$	$y$	$z$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{12}$	$U_{13}$	$U_{23}$
C(1)	7179 (4)	6536 (4)	2763 (4)	45 (3)	32 (2)	59 (3)	7 (2)	4 (2)	6 (2)
C(2)	6156 (4)	7011 (4)	2560 (5)	56 (3)	43 (2)	73 (4)	17 (2)	-12 (3)	12 (3)
C(3)	5336 (4)	6195 (5)	2670 (6)	52 (3)	59 (3)	95 (5)	22 (7)	-33 (3)	-13 (3)
C(4)	5427 (3)	5389 (3)	3698 (5)	28 (2)	36 (2)	80 (4)	1 (2)	-7 (2)	-15 (2)
C(5)	6462 (3)	4904 (3)	3630 (4)	30 (2)	31 (2)	38 (3)	-3 (2)	-1 (2)	-7 (2)
C(6)	6647 (3)	3938 (3)	4451 (4)	37 (2)	30 (2)	52 (3)	-8 (2)	4 (2)	-3 (2)
C(7)	7637 (3)	3459 (3)	4168 (4)	38 (2)	23 (2)	54 (3)	-5 (2)	-2 (2)	0 (2)
C(8)	8425 (3)	4284 (3)	4015 (4)	34 (2)	28 (2)	45 (3)	2 (2)	-2 (2)	-1 (2)
C(9)	8251 (3)	5322 (3)	3973 (4)	28 (2)	29 (2)	41 (3)	0 (2)	0 (2)	1 (2)
C(10)	7223 (3)	5798 (3)	3886 (4)	25 (2)	25 (2)	47 (2)	1 (1)	1 (2)	0 (2)
C(11)	9110 (3)	6047 (3)	4055 (5)	32 (2)	32 (2)	59 (3)	3 (2)	0 (2)	-3 (2)
C(12)	10132 (3)	5598 (3)	3943 (5)	29 (2)	36 (2)	70 (3)	-1 (2)	-1 (2)	-6 (2)
C(13)	10303 (3)	4558 (3)	3859 (5)	36 (2)	37 (2)	58 (3)	4 (2)	-2 (2)	-7 (2)
C(14)	9451 (3)	3849 (3)	3946 (5)	37 (2)	32 (2)	60 (3)	4 (2)	0 (2)	1 (2)
C(15)	11321 (3)	4079 (4)	3747 (6)	33 (2)	37 (2)	96 (4)	4 (2)	4 (3)	-10 (3)
C(16)	11841 (4)	4437 (5)	2604 (5)	54 (3)	79 (4)	74 (4)	9 (3)	2 (3)	-24 (3)
C(17)	11941 (4)	4281 (5)	4853 (6)	57 (3)	83 (4)	83 (4)	24 (3)	0 (3)	12 (4)
C(18)	4626 (4)	4549 (5)	3543 (7)	40 (3)	55 (3)	146 (7)	-6 (3)	-21 (4)	-29 (4)
C(19)	5288 (3)	5897 (4)	4944 (5)	32 (2)	39 (2)	80 (4)	-1 (2)	10 (2)	-7 (3)
C(20)	6996 (3)	6417 (3)	5068 (4)	32 (2)	29 (2)	45 (3)	0 (2)	-1 (2)	-5 (2)
O(21)	7572 (2)	2842 (2)	3067 (3)	47 (2)	28 (1)	58 (2)	1 (1)	3 (2)	-6 (1)
O(22)	9038 (2)	6992 (2)	4187 (4)	36 (2)	28 (1)	134 (3)	-3 (1)	4 (2)	-17 (2)
O(23)	10857 (2)	6301 (2)	3934 (5)	29 (2)	39 (2)	136 (3)	0 (1)	7 (2)	-23 (2)
O(24)	9558 (2)	2886 (2)	3950 (4)	45 (2)	29 (1)	119 (3)	7 (1)	3 (2)	-19 (2)
O(25)	5987 (2)	6729 (2)	5156 (3)	35 (1)	39 (1)	48 (2)	3 (1)	5 (1)	-10 (1)
O(26)	7283 (3)	5833 (3)	6073 (3)	73 (2)	45 (2)	46 (2)	14 (2)	-12 (2)	0 (2)

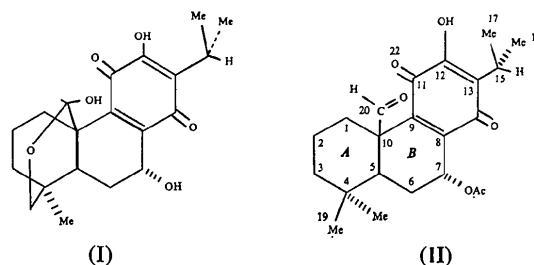
Table 2 (cont.)

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1 <i>a</i> )	728	600	200	3.0†
H(1 <i>b</i> )	758	713	293	
H(2 <i>b</i> )	598	758	304	
H(2 <i>a</i> )	605	741	177	
H(3 <i>a</i> )	537	572	198	
H(3 <i>b</i> )	476	649	270	
H(5)	659	463	290	
H(6 <i>a</i> )	618	347	428	
H(6 <i>b</i> )	660	437	531	
H(7)	785	296	484	
H(15)	1119	336	368	
H(16 <i>a</i> )	1160	428	197	
H(16 <i>b</i> )	1253	400	261	
H(16 <i>c</i> )	1199	513	259	
H(17 <i>a</i> )	1201	500	500	
H(17 <i>b</i> )	1255	388	487	
H(17 <i>c</i> )	1165	411	567	
H(18 <i>a</i> )	476	401	275	
H(18 <i>b</i> )	468	405	422	
H(18 <i>c</i> )	404	500	334	
H(19 <i>a</i> )	467	633	500	
H(19 <i>b</i> )	537	536	553	
H(20)	734	705	500	
H(21)	798	247	304	
H(23)	1061	684	396	

† H atomic ( $\times 10^3$ ) and thermal (*B*) parameters not refined. The value of  $B=3.0$  was assigned to each H atom. H(26) could not be located in difference Fourier maps.

II, isolated from *Salvia nemorosa* (Romanova, Pribylova, Zakharov, Sheichenko & Ban'lovshii, 1971). Hypothetically, the two structures are related by oxidation of the  $\beta$ -methyl group at C(4) of nemorone followed by

formation of the hemiacetal. The C(7) ester is lost easily by hydrolysis. Although only the relative absolute configuration was determined in this X-ray investigation, the absolute configuration is known. The stereochemistry is determined by that of the *A:B trans* ring juncture (Hanson, 1972).



Ring *A* and the hemiacetal ring *A'* exhibit distorted chair conformations while ring *B* is a distorted half-chair (Romers, Altona, Jacobs & de Graaff, 1974). The quinone ring *C* is not planar and is described best as being folded about a line defined by atoms (10)–(9)–(13)–(15). The folding of the quinone ring places O(22) between the H atoms of C(1) and C(20). This is reflected in the O(22)–H(1) and O(22)–H(20) distances of 2.43 and 2.48 Å and the C(1)C(10)C(9)C(11) and C(20)C(10)C(9)C(11) torsion angles of +57 and –64°. The C(16) and C(17) methyl groups are bisected by the quinone ring giving torsion angles of C(12)C(13)C(15)C(16) = –62° and C(12)C(13)C(15)C(17) = 64°. The two C=O distances in the quinone are consistent with literature values (*Molecular Structures*

Table 3. Bond distances (Å) and angles (°)

The estimated standard deviations of the angles range from 0.3 to 0.5°.

C(1)–C(2)	1.533 (7)	C(20)–O(26)	1.382 (5)	C(14)–C(8)	1.503 (6)
C(2)–C(3)	1.527 (8)	C(5)–C(6)	1.539 (6)	C(7)–O(21)	1.440 (5)
C(3)–C(4)	1.526 (8)	C(6)–C(7)	1.510 (6)	C(11)–O(22)	1.209 (5)
C(4)–C(5)	1.539 (6)	C(7)–C(8)	1.507 (6)	C(14)–O(24)	1.229 (5)
C(5)–C(10)	1.561 (6)	C(8)–C(9)	1.337 (5)	C(12)–O(23)	1.330 (5)
C(10)–C(1)	1.545 (6)	C(9)–C(10)	1.527 (5)	C(13)–C(15)	1.519 (6)
C(4)–C(19)	1.520 (8)	C(9)–C(11)	1.490 (6)	C(15)–C(16)	1.507 (8)
C(19)–O(25)	1.439 (6)	C(11)–C(12)	1.510 (6)	C(15)–C(17)	1.498 (9)
O(25)–C(20)	1.433 (5)	C(12)–C(13)	1.341 (6)	C(4)–C(18)	1.533 (7)
C(20)–C(10)	1.545 (6)	C(13)–C(14)	1.470 (6)		
C(1)C(2)C(3)	112.8	C(10)C(5)C(6)	111.3	C(9)C(11)O(22)	123.6
C(2)C(3)C(4)	116.8	C(5)C(6)C(7)	110.2	C(12)C(11)O(22)	117.2
C(3)C(4)C(5)	107.8	C(6)C(7)C(8)	112.4	C(7)C(8)C(14)	114.5
C(4)C(5)C(10)	108.1	C(7)C(8)C(9)	124.0	C(8)C(14)O(24)	118.2
C(5)C(10)C(1)	105.6	C(8)C(9)C(10)	123.6	C(13)C(14)O(24)	120.9
C(10)C(1)C(2)	112.9	C(9)C(10)C(5)	109.5	C(11)C(12)O(23)	115.7
C(5)C(4)C(19)	109.1	C(9)C(10)C(20)	109.4	C(13)C(12)O(23)	122.0
C(4)C(19)O(25)	111.9	C(6)C(7)O(21)	109.5	C(12)C(13)C(15)	123.8
C(19)O(25)C(20)	115.0	C(8)C(7)O(21)	109.1	C(14)C(13)C(15)	118.8
O(25)C(20)C(10)	112.8	C(8)C(9)C(11)	117.7	C(13)C(15)C(16)	112.1
C(20)C(10)C(5)	112.7	C(9)C(11)C(12)	119.1	C(13)C(15)C(17)	112.4
C(20)C(10)C(1)	110.6	C(11)C(12)C(13)	122.4	C(16)C(15)C(17)	110.8
O(25)C(20)O(26)	111.4	C(12)C(13)C(14)	117.3	C(19)C(4)C(18)	107.7
O(26)C(20)C(10)	109.8	C(13)C(14)C(8)	120.9	C(5)C(4)C(18)	111.7
C(3)C(4)C(19)	111.6	C(14)C(8)C(9)	121.5	C(10)C(9)C(11)	118.7
C(3)C(4)C(18)	109.0	C(1)C(10)C(9)	108.9	C(4)C(5)C(6)	116.0

Table 4. Torsion angles for conacytone (°)

Internal		Ring A		Ring A'		Ring B		Ring C	
(1)–(2)	–46	(20)–(25)	+50	(6)–(7)	+43	(13)–(14)	+5		
(2)–(3)	+41	(25)–(19)	–57	(7)–(8)	–8	(14)–(8)	+2		
(3)–(4)	–50	(19)–(4)	+61	(8)–(9)	–9	(8)–(9)	–10		
(4)–(5)	+64	(4)–(5)	–57	(9)–(10)	–10	(9)–(11)	+11		
(5)–(10)	–69	(5)–(10)	+51	(5)–(10)	+45	(11)–(12)	–5		
(10)–(1)	+60	(10)–(20)	–47	(5)–(6)	–63	(12)–(13)	–3		
External									
(22)–(11)–(12)–(23)	–4	(11)–(9)–(10)–(20)	–64	(6)–(5)–(4)–(19)	+69				
(22)–(11)–(9)–(10)	+8	(14)–(13)–(15)–(17)	–113	(1)–(10)–(20)–(26)	–165				
(24)–(14)–(13)–(15)	+1	(14)–(13)–(15)–(16)	+122	(12)–(13)–(15)–(16)	–62				
(24)–(14)–(8)–(7)	+4	(12)–(13)–(15)–(17)	+64	(9)–(10)–(20)–(26)	–45				
(14)–(8)–(7)–(21)	–68	(6)–(5)–(4)–(18)	–50	(5)–(10)–(20)–(26)	+77				
(11)–(9)–(10)–(1)	+57	(6)–(5)–(4)–(3)	–170	(19)–(25)–(20)–(26)	–74				

and Dimensions, 1972), and the C(12)–O(23) distance of 1.330 (5) Å agrees with those found in hydroxy substituted quinones such as tetrahydro-*p*-benzoquinone (Klug, 1965). The C–hydroxyl O distance, C(20)–O(26) of 1.382 (5) Å is similar to values reported for carbohydrate hemiacetals. The C(19)–O(25) and C(20)–O(25) distances of 1.439 (6) and 1.433 (5) Å are normal. In general, the bond distances and bond angles indicate little steric strain in the molecule.

Two close intermolecular contacts, O(23)–O(25)\* = 2.69 and O(21)–O(26)\* = 2.76 Å, indicate strong hydrogen bonding. The peak search program located H(23) at 0.76 Å from O(23) and 2.1 Å from O(25'). The H atom associated with O(26) could not be found in the difference Fourier map. H(21) is involved in an intramolecular hydrogen bond with O(24), O(21)–O(24) = 2.9 Å while H(23) also is involved in an intramolecular interaction with O(22), O(23)–O(22) = 2.64 and O(22)–H(23) = 2.16 Å.

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\* O(25') = (½ + x, ½ – x, z̄); O(26') = (½ – x, ȳ, ½ + z).

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