

One may expect, therefore, that these sites would have a tendency towards the geometry of the PtS or cooperite structure. This is, in fact, the case with the 4(*j*) site forming what is essentially a cooperite-like subcell ($a \approx 3.3$, $c \approx 6.6$ Å) within the cell of braggite (see Fig. 1). The cooperite-like subcell is considerably twisted with respect to the braggite cell axes but, nevertheless, this type of coordination is entirely consistent with the placement of (Pt, Ni) atoms at the 4(*j*) site. It also follows that the presence of a cooperite-like subcell supports the placement of Pd atoms at the 2(*d*) sites since these sites are quite distinct from this subcell arrangement. This relationship between the braggite and cooperite structures should contribute to a better understanding of the Pt-Pd-S system.

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The Crystal Structure of the Sesquiterpene (–)-Aristolone

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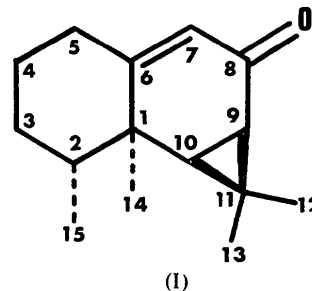
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Crystals of the sesquiterpene (–)-aristolone, $C_{15}H_{22}O$, are trigonal, space group $P3_2$, $a = 11.782$ (1), $c = 8.286$ (1) Å, $Z = 3$. The structure has been solved by a direct phasing technique using diffractometer data, and refined to $R = 0.055$. The structure solution indicates the sensitivity of the procedure employed to small changes in the criteria for acceptance of new phase indications. A feature of the structure is the hyperconjugation between the cyclopropane ring and an adjacent carbonyl group, resulting in the shortening to 1.439(10) Å of the C(sp^3)–C(sp^2) bond linking the two groups.

Introduction

The sesquiterpene aristolone was first isolated by Kariyone & Naito (1955) from *Aristolchia debilis* Sieb. et Zucc. In a series of papers (Furukawa & Soma, 1961; Furukawa, Oyamada & Soma, 1961; Furukawa, 1961) the molecule was shown to have the chemical formula $C_{15}H_{22}O$ and the structure (I) (which also indicates the numbering adopted in this study). The absolute stereochemistry depicted in (I) is that of (–)-aristolone, determined by indirect correlation with the known absolute configuration of maaliol (Büchi, Greuter & Tokoroyama, 1962). The correctness of the structural assignment was confirmed by the total synthesis of

(±)-aristolone by two independent routes (Piers, Britton & de Waal, 1969a; Berger, Franck-Neumann & Ourisson, 1968).



(I)

The crystal data for (–)-aristolone were first determined (by F. H. A. and J. T.) during a survey of compounds with which the effect of anomalous dispersion

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of X-rays by oxygen might be studied. While it was considered that the proportion of oxygen was not sufficient for this purpose, a three-dimensional X-ray analysis was carried out since the structure contained some interesting geometrical features and the novel application of direct methods to space group $P3_1/P3_2$ was of crystallographic interest.

Experimental

Crystals of (-)-aristolone are large, well-formed, colourless rhombs. The symmetry and space group were determined from oscillation and Weissenberg photographs taken about the a and c axes. Cell parameters were obtained by least-squares refinement of the 2θ -values of 23 general ($h, k, l \neq 0$), high order ($2\theta > 65^\circ$) reflexions, measured on a diffractometer.

Crystal data

(-)-Aristolone: $C_{15}H_{22}O$; $M = 218.4$, hexagonal (trigonal) $a = 11.782$ (1), $c = 8.286$ (1) Å, $U = 996.1$ Å³, $D_m = 1.07 \pm 0.03$ g cm⁻³ (by flotation), $Z = 3$, $D_x = 1.092$ g cm⁻³. Absorption coefficient (μ) = 10.72 cm⁻¹, for Cu $K\alpha$ radiation ($\lambda_{\text{mean}} = 1.54178$ Å). $F(000) = 360$. The absent spectra $00l$, $l \neq 3n$ define the space group as $P3_1(C_3^2, \text{No. 145})$ or $P3_2(C_3^2, \text{No. 146})$, the latter is indicated by the known absolute configuration.

The intensity data were collected on a Datex-automated G. E. XRD6 diffractometer, using Ni-filtered Cu $K\alpha$ radiation. The θ - 2θ scan technique was used at a speed of 2° (2θ) per min, with background counting for 20 sec at the scan limits. A roughly spherical specimen, of mean diameter 0.4 mm, was mounted with c parallel to the φ axis of the goniostat. 985 independent reflexions with $2\theta < 120^\circ$ were scanned. A 'check' reflexion was monitored after each batch of 25 data, and the corrected scan count ($S-B$, where B is the background count corrected to scan time) for this reflexion was used to place the data batches on a common scale. The value of $S-B$ for the monitor varied by $\pm 4\%$ during the experiment and the applied scale factor ranged from 0.991 to 1.083. Using the expression

$$\sigma^2(I) = S + B + (0.05S)^2,$$

111 reflexions for which the ratio $I/\sigma(I) \leq 3.0$ were classified as unobserved. Absorption corrections were not applied and structure amplitudes were derived in the usual manner.

Structure determination and refinement

The data were placed on an approximately absolute scale by Wilson's (1942) method, and $|E|$ values obtained using the program of Hall (1967). The $|E|$ statistics derived are compared with the theoretical values (Karle, Dragonette & Brenner, 1965) for centrosymmetric and non-centrosymmetric distributions in Table 1.

Table 1. E -statistics for (-)-aristolone

	Experimental	Theoretical	
	(-)-aristolone	Centro	Non-centro
$\langle E \rangle$	0.866	0.798	0.886
$\langle E ^2 \rangle$	0.988	1.000	1.000
$\langle E^2 - 1 \rangle$	0.763	0.968	0.736
$ E \geq 3.0(\%)$	0.20	0.30	0.01
$ E \geq 2.0(\%)$	2.74	5.00	1.80
$ E \geq 1.0(\%)$	33.91	32.00	37.00

The structure was solved by direct methods based on the 155 values of $|E| \geq 1.30$. The rules for origin definition in space groups $P3_1$ and $P3_2$ allow two reflexions ($\mathbf{h}_1, \mathbf{h}_2$) to have arbitrary phases (φ):

(i) $\varphi(\mathbf{h}_1) = 0$ for a reflexion with $h \equiv k \pmod{3}$ and $l = \pm 1$,

(ii) $0 \leq \varphi(\mathbf{h}_2) < \pi/3$ for a reflexion with $h \equiv k \pmod{3}$ and $l = 0$.

It was not possible to satisfy (ii) with a reflexion of high $|E|$ that entered into many \sum_2 relationships, although criterion (i) was satisfied by 391 ($|E| = 2.67$). This reflexion was given $\varphi = 0$ and input with the other 154 data to a program (Motherwell & Isaacs 1971) which selects reflexions to be given symbolic phases in the tangent-formula refinement. Two reflexions with $|E| > 2.0$ were selected by this method and given phase values a and b (see Table 2).

Table 2. 'Starting set' of reflexions for tangent-formula phase refinement

\mathbf{h}	$ E(\mathbf{h}) $	$\varphi(\mathbf{h})$
3 -9 -1	2.67	0 (fixed for origin definition)
2 -8 -3	3.08	$a = \pm \pi/4, \pm 3\pi/4$
5 2 5	2.63	$b = \pm \pi/4, \pm 3\pi/4$
*4 3 5	1.99	$c = 0 < \varphi(\mathbf{h}) < 2\pi/3$

* Included after run 1 (Table 3), see text.

The basic set of reflexions of Table 2 was used to initiate phase determination and refinement in a program (Kennard *et al.*, 1972) which employs iterative application of the tangent formula (Karle & Hauptmann, 1956):

$$\tan \varphi(\mathbf{h}) =$$

$$\frac{\sum_{\mathbf{k}} |E(\mathbf{k})| \cdot E(\mathbf{h} - \mathbf{k}) \cdot \sin \varphi(\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k})}{\sum_{\mathbf{k}} |E(\mathbf{k})| \cdot E(\mathbf{h} - \mathbf{k}) \cdot \cos \varphi(\mathbf{k}) + \varphi(\mathbf{h} - \mathbf{k})} \approx A/B.$$

The program will accept up to 20 fixed phases (origin, enantiomorph, \sum_1 -type, *etc*) and up to three symbolic assignments. The symbolic phases are systematically assigned specified numerical starting values, and phase sets are calculated for all combinations of the starting values. For each estimated phase a consistency index (t), and the parameter (α) (Karle & Karle, 1966), are calculated where:

$$t = (A^2 + B^2)^{1/2} / \sum_{\mathbf{k}} |E(\mathbf{k})| \cdot |E(\mathbf{h} - \mathbf{k})| (0 < t < 1);$$

and

$$\alpha = 2\sigma_3\sigma_2^{-3/2} \cdot |E(\mathbf{h})| \cdot (A^2 + B^2)^{1/2}$$

where

$$\sigma_n = \sum_{j=1}^N Z_j^n$$

and Z_j is the atomic number of the j th atom in a unit cell containing N atoms.

A phase indication is accepted if it satisfies the following criteria:

(i) The value of φ does not change by more than a specified amount (usually $\pi/2$) from cycle to cycle. The cycling procedure is explained below.

(ii) $t > t_{\min}$, where the minimum consistency is usually 0.25.

(iii) $\alpha > \alpha_{\min}$, following the graph of variance of phase angle (σ_φ) vs. α (Karle & Karle, 1966). The value of α_{\min} is usually set at 2.5 equivalent to $\sigma_\varphi \approx 40^\circ$.

(iv) A phase indication from a single triple product interaction is only accepted if all three contributing $|E|$ values exceed $|E|_{\min}$, usually set at 2.0.

Finally for each phase set an R index is calculated by the procedure of Karle & Karle (1966). We have found that R_{Karle} is the best single indicator of the most probable correct phase set. In the non-centrosymmetric case values in the range 0.18–0.25 often lead to the correct

structure and are easily distinguished from incorrect sets with values above 0.30.

The structure-solution procedure for (–)-aristolone is summarized in some detail in Table 3, since it indicates the sensitivity of the method to small changes in the acceptance criteria t_{\min} , $|E|_{\min}$ and α_{\min} . In all runs the cycling procedure was as follows: the first 50 reflexions (in decreasing order of $|E|$) were refined for 5 cycles, the first 100 for the next 10 cycles, and all 155 data for the final 10 cycles, making 25 cycles in all for each starting set. The symmetry of space group $P3_1$ was used throughout. The sixteen values of R_{Karle} for run 1 were all in the range 0.29–0.31, but a feature was the low value of $|E|_{\text{calc}}$ (see Karle & Karle, 1966) for the 435 reflexion ($|E|_{\text{obs}} = 1.99$) in most phase sets. This reflexion entered into many \sum_2 interactions and was included in subsequent runs as symbolic phase c with initial numeric phase assignments limited to the range $0 < \varphi(\mathbf{h}) < 2\pi/3$. The initial method of attack was to increase α_{\min} but from the results of Table 3 it is obvious that an inconsistency in the early stages of expansion and refinement satisfied the criteria until t_{\min} was raised to 0.30.

Phase set 12 of run 5 was refined for a further five cycles to an R_{Karle} of 0.175. The strongest 35 peaks of the resultant E map were located automatically and their interpolated positions input to a computer program (written by Dr W. D. S. Motherwell) which uses space-group symmetry and a maximum bond-length value to assemble unique bonded fragments; the information so assembled was then plotted on-line. Of the strongest 21 peaks only two (numbers 19 and 20) were spurious and 19 were found to belong to a unique 16-atom fragment or to its symmetry related counterparts.

The structure was refined by full-matrix least-squares methods. Scattering factors for C and O were taken from *International Tables for X-ray Crystallography* (1962), and those for H from Stewart, Davidson & Simpson (1965). Refinement of the carbon and oxygen

Table 3. Phase refinement procedure for (–)-aristolone

Run	Initial values for c^\dagger		$ E _{\min}$	t_{\min}	α_{\min}	min. R_{Karle} (%)	Set No.
1	–	–	2.00	0.25	2.50	–	–
						27.7	26
2	80	160	2.00	0.25	3.00	27.8	12
						28.5	15
3*	80	240	2.00	0.25	3.25	29.3	12
4	80	240	2.00	0.30	3.25	26.5	12
5	80	240	2.00	0.30	3.25	17.7	12

* The 110 reflexion was omitted for this run only as it was suspected of causing inconsistencies.

† Values in millicycles (mc), $2\pi = 1000\text{mc}$.

Table 4. Final parameters ($\times 10^4$) for the non-hydrogen atoms (standard deviations in parentheses)

Anisotropic temperature factors are of the form:–

$$f = f_0 \exp [-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
O(1)	11964 (5)	8784 (5)	–648 (8)	224 (6)	151 (5)	225 (7)	68 (5)	78 (6)	62 (5)
C(1)	10143 (5)	7455 (5)	3872	116 (5)	105 (5)	133 (7)	57 (4)	2 (5)	–7 (5)
C(2)	9445 (6)	6136 (5)	4825 (7)	145 (6)	117 (6)	137 (8)	42 (5)	18 (5)	2 (5)
C(3)	10255 (8)	6126 (6)	6245 (8)	232 (11)	151 (7)	143 (9)	75 (7)	–18 (7)	13 (7)
C(4)	11582 (8)	6391 (7)	5713 (10)	223 (11)	171 (9)	256 (13)	98 (8)	–89 (10)	10 (8)
C(5)	12297 (6)	7674 (7)	4868 (9)	132 (7)	160 (8)	273 (11)	66 (6)	–55 (7)	–13 (8)
C(6)	11509 (5)	7767 (4)	3472 (8)	99 (5)	85 (4)	191 (9)	33 (4)	–17 (5)	–12 (5)
C(7)	12042 (5)	8146 (5)	1994 (9)	100 (6)	123 (6)	252 (11)	37 (5)	6 (6)	1 (6)
C(8)	11376 (6)	8289 (5)	610 (8)	152 (7)	91 (5)	186 (8)	50 (5)	36 (6)	13 (6)
C(9)	10002 (6)	7858 (5)	764 (8)	184 (8)	125 (6)	162 (8)	102 (6)	–14 (6)	21 (5)
C(10)	9350 (5)	7357 (5)	2375 (8)	108 (5)	140 (6)	165 (8)	77 (5)	4 (5)	–15 (5)
C(11)	9000 (5)	6401 (5)	1012 (8)	112 (5)	138 (6)	143 (7)	50 (5)	–15 (5)	–2 (5)
C(12)	9471 (6)	5416 (5)	899 (8)	179 (7)	96 (5)	160 (8)	54 (5)	2 (6)	–7 (5)
C(13)	7684 (7)	5947 (10)	279 (10)	146 (8)	283 (14)	220 (11)	74 (9)	–61 (8)	–34 (10)
C(14)	10264 (7)	8619 (6)	4864 (9)	217 (9)	150 (7)	193 (10)	111 (7)	–8 (8)	–45 (7)
C(15)	8029 (8)	5764 (10)	5337 (11)	152 (9)	296 (14)	253 (13)	57 (9)	86 (9)	25 (10)

positions from the E map, together with individual isotropic thermal parameters and an overall scale factor reduced R for the observed data from 0.378 to 0.143. The introduction of anisotropic thermal parameters reduced R to 0.072. The weighting scheme employed was that due to Hughes (1941) where:

$$w=1 \text{ for } |F_o| \leq F^*$$

$$w=F^*/|F_o| \text{ for } |F_o| > F^*$$

with F^* set to 6.5 on the absolute scale. Four strong, low-order reflexions found to suffer seriously from secondary extinction effects were given zero weight.

The non-methyl hydrogen atoms were located in a difference map, and their positional isotropic thermal parameters were included in the refinement; R fell to 0.062. A second difference map gave the positions of the methyl hydrogens at C(13) and C(14) and they were included in refinement as before. The R index for the observed data fell to 0.055, and to 0.061 for all data. A final difference map failed to reveal the positions of the methyl hydrogens at C(12) and C(15); refinement was concluded, the maximum positional shift on the final cycle being 0.009 Å. The final fractional coordinates and thermal parameters are in Tables 4 and 5, observed and calculated structure factors are listed in Table 6.

Table 5. Final fractional coordinates ($\times 10^3$) and B values (\AA^2) for the hydrogen atoms

	x	y	z	B
H(21)	948 (8)	552 (8)	387 (9)	5.9 (17)
H(31)	954 (11)	512 (12)	686 (14)	5.8 (28)
H(32)	1028 (10)	685 (10)	708 (15)	12.4 (24)
H(41)	1147 (12)	564 (12)	488 (13)	5.1 (28)
H(42)	1208 (11)	652 (10)	673 (13)	12.1 (25)
H(51)	1304 (10)	777 (9)	437 (10)	10.5 (21)
H(52)	1237 (8)	834 (9)	559 (10)	7.1 (20)
H(71)	1276 (10)	810 (9)	174 (10)	9.4 (22)
H(91)	972 (7)	826 (7)	23 (8)	5.2 (14)
H(101)	877 (8)	742 (7)	256 (9)	7.2 (16)
H(131)	711 (6)	523 (6)	92 (8)	10.2 (15)
H(132)	753 (6)	549 (6)	-71 (8)	12.4 (14)
H(133)	772 (7)	671 (6)	8 (7)	12.4 (15)
H(141)	1091 (5)	940 (5)	411 (6)	10.2 (11)
H(142)	949 (5)	846 (5)	533 (6)	11.7 (11)
H(143)	1078 (5)	870 (5)	581 (6)	7.1 (11)

Discussion

A perspective view of the molecule is shown in Fig. 1, and confirms the structure assigned chemically. No attempt was made to determine the absolute configuration since the proportion of oxygen present, and the

accuracy attained, were not high enough to guarantee the result. The absolute stereochemistry appears to be well established by chemical techniques (Büchi, Greuter & Tokoroyama, 1962; Piers, Britton & de Waal, 1969b), and this result was used to assign the true space group as $P3_2$.

Final bond lengths and angles are in Tables 7 and 8, and intraannular torsion angles are in Fig. 2. Details of mean planes referred to below are given in Table 9.

The most interesting structural feature is the presence of the fused cyclopropane ring adjacent to the carbonyl group. It is well known that cyclopropane has chemical

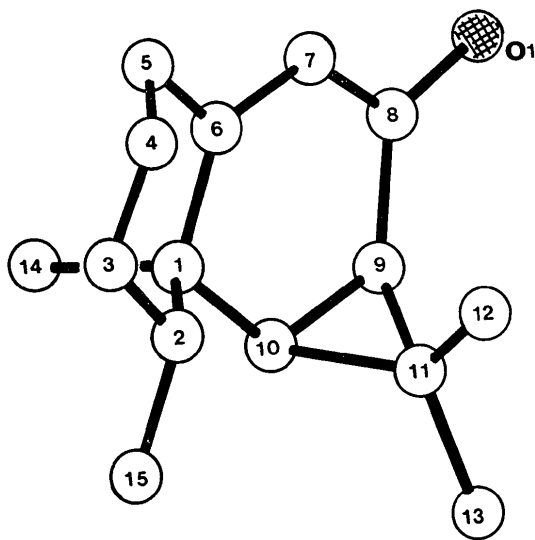


Fig. 1. Perspective view of a molecule of (-)-aristolone showing the chemically deduced absolute stereochemistry.

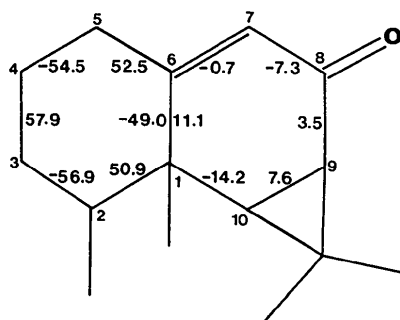


Fig. 2. Intra-annular torsion angles in the two six-membered rings. Standard deviations (Huber, 1961) range from 0.6–0.8°.

Table 6. Observed and calculated structure factors ($\times 10$)

Unobserved reflexions have negative $|F_o|$. Reflexions omitted for suspected extinction were

h	k	l	$ F_o $	$ F_c $
0	2	0	379	466
1	1	0	566	860
1	0	1	260	518
0	1	2	339	620

Table 6 (cont.)

H ⁻¹ K ^a 11	H ⁻² K ^a 8	H ⁻³ K ^a 4	H ⁻⁵ K ^a 7	H ⁻⁸ K ^a 11	H ⁰ K ^a 7	H ¹ K ^a 6	H ² K ^a 9	H ³ K ^a 11	H ⁴ K ^a 5	H ⁵ K ^a 5	H ⁷ K ^a 3
3 -6 9	5 0 7	8 14 12	5 18 18	4 -6 8	3 58 58	0 -15 11	3 34 30	7 53 55	2 55 55	0 22 20	
2 18 22	4 48 49	7 14 13	4 18 13	3 20 22	4 107 107	1 42 46	4 25 26	8 25 26	3 36 37	1 26 26	
1 23 25	3 179 184	6 30 34	3 37 55	2 46 46	5 20 20	2 46 46			4 50 51	2 24 22	
2 102 97	5 47 49	2 47 53	2 47 53	1 -14 16	6 30 27	3 -14 5	H ² K ^a 10	H ⁴ K ^a 2	5 32 34	3 56 56	
H ⁻¹ K ^a 10	1 56 56	4 45 47	1 -6 7	H ⁻⁸ K ^a 10	7 11 8	4 42 44			6 29 27	4 31 28	
5 -9 5	H ⁻² K ^a 7	2 76 75	H ⁻⁵ K ^a 6	H ⁻⁸ K ^a 10	H ⁰ K ^a 8	6 -7 6	1 23 21	0 152 158	H ³ K ^a 6	5 20 22	
4 -5 3	1 219 214	8 -3 8	5 24 24					2 117 108	4 32 33	H ⁷ K ^a 4	
3 18 19	7 21 21	8 -3 8	5 24 24					3 113 119	0 46 43		
2 43 42	6 29 29	H ⁻⁴ K ^a 12	7 39 37	3 -13 13	0 23 24	H ¹ K ^a 9	H ³ K ^a 0	4 117 100	1 36 39	0 43 39	
1 65 61	5 22 27		6 35 37	2 32 38	2 48 39	0 29 25	1 93 103	5 37 40	2 25 25	1 28 26	
H ⁻¹ K ^a 9	4 37 81	3 29 29	5 29 35	1 40 40	3 36 37	1 -15 15	2 165 146	6 36 36	1 15 16	2 16 40	
6 13 15	3 27 40	7 24 26	6 30 35	H ⁻⁸ K ^a 9	5 -12 13	3 32 35	4 102 85	0 26 24	5 18 18	4 24 24	
5 14 17	2 103 98	1 -8 9	3 103 105	H ⁻⁸ K ^a 9	6 14 12	4 19 22	5 166 164	0 59 59	H ² K ^a 7	5 12 17	
3 80 80	1 154 155	H ⁻⁴ K ^a 11	1 121 115	5 17 16	H ⁰ K ^a 9	7 -10 10	6 59 59	7 50 55	H ² K ^a 7	H ⁷ K ^a 5	
2 -16 11	8 13 13	5 11 9	H ⁻⁶ K ^a 13	4 16 14	3 45 50	H ¹ K ^a 10	8 28 26	0 72 72	0 -8 8	0 -11 11	
1 61 65	7 26 26	3 16 16	1 -5 3	2 51 50	1 50 53	0 19 18	H ³ K ^a 1	1 50 56	1 16 15	1 19 19	
H ⁻¹ K ^a 8	6 41 43	2 -11 13	H ⁻⁵ K ^a 12	1 27 25	2 30 30	1 29 29	1 32 30	3 32 30	3 -9 8	2 31 29	
7 -8 10	5 38 41	1 28 35	H ⁻⁵ K ^a 12	1 19 20	1 19 20	2 27 27	0 257 232	4 99 94	H ² K ^a 8	3 21 21	
6 -10 10	4 43 44	3 25 25	H ⁻⁹ K ^a 12	5 20 21	5 20 21	3 17 17	1 60 65	5 114 125	H ² K ^a 8	H ⁷ K ^a 6	
5 29 31	3 95 96	H ⁻⁴ K ^a 10	3 25 25	3 -6 6	H ⁰ K ^a 10	H ² K ^a 0	3 52 47	7 16 14	0 10 5	0 20 21	
4 91 96	2 157 160	6 -7 11	2 -10 13	2 28 25	2 28 25	2 21 18	4 18 21	4 11 12	2 5 2	1 19 19	
3 46 45	1 131 140	5 31 29	1 16 17	1 -6 17	H ⁰ K ^a 10	1 27 25	2 30 30	1 29 29	3 32 30	3 21 21	
2 119 123	8 30 33	4 -8 13	H ⁻⁶ K ^a 11	3 -6 6	H ⁰ K ^a 10	0 0 15	2 295 264	6 75 74	H ² K ^a 0	H ⁸ K ^a 0	
H ⁻¹ K ^a 7	6 21 21	3 49 50	5 30 28	H ⁻⁹ K ^a 11	1 24 28	3 124 115	-7 17 18	0 57 50			
6 32 36	3 49 50	6 -7 11	2 -10 13	4 14 11	3 124 115	7 17 18	0 57 50	1 76 75	1 15 16		
5 -5 15	1 170 169	4 -11 6	H ⁻⁶ K ^a 10	3 16 13	4 14 11	3 21 20	5 59 58	2 79 61	2 161 155	2 52 54	
4 67 66	3 49 50	2 46 47	2 46 47	4 16 13	4 25 23	6 66 63	H ³ K ^a 2	3 41 41	3 47 42	3 58 55	
3 26 26	H ⁻² K ^a 4	3 128 131	6 22 18	2 24 26	2 24 26	2 40 47	8 40 43	4 53 58	4 89 89	4 57 63	
2 33 36	6 39 40	2 96 99	5 -8 11	4 21 17	4 21 17	2 40 47	8 40 43	4 53 58	4 89 89	4 57 63	
1 92 88	6 45 42	1 45 47	4 -11 15	1 18 20	H ⁰ K ^a 11	1 18 20	H ⁰ K ^a 11	7 40 36	0 118 112	6 -17 17	
H ⁻¹ K ^a 6	6 39 40	2 96 99	5 -8 11	1 31 31	H ⁰ K ^a 11	1 18 20	H ⁰ K ^a 11	7 40 36	0 118 112	6 -17 17	
8 26 24	4 80 80	7 15 16	4 -11 15	4 21 17	H ⁰ K ^a 11	1 18 20	H ⁰ K ^a 11	7 40 36	0 118 112	6 -17 17	
7 34 33	3 187 177	6 18 21	H ⁻⁶ K ^a 10	4 21 17	H ⁰ K ^a 11	1 18 20	H ⁰ K ^a 11	7 40 36	0 118 112	6 -17 17	
6 46 47	2 109 112	5 -19 22	6 12 11	4 21 17	H ⁰ K ^a 11	1 18 20	H ⁰ K ^a 11	7 40 36	0 118 112	6 -17 17	
5 39 39	1 224 195	3 75 72	5 18 17	4 21 17	H ⁰ K ^a 11	1 18 20	H ⁰ K ^a 11	7 40 36	0 118 112	6 -17 17	
4 94 98	3 33 35	H ⁻² K ^a 3	3 91 92	4 -9 6	H ⁻¹⁰ K ^a 11	9 15 15	3 75 78	3 65 60	H ² K ^a 6	0 70 71	
3 111 115	1 136 134	8 23 22	2 71 77	2 -7 6	H ⁻¹⁰ K ^a 11	9 15 15	3 75 78	3 65 60	H ² K ^a 6	0 70 71	
2 136 134	8 23 22	2 71 77	2 71 77	3 -6 10	H ⁻¹⁰ K ^a 11	9 15 15	3 75 78	3 65 60	H ² K ^a 6	0 70 71	
H ⁻¹ K ^a 5	8 37 36	H ⁻⁴ K ^a 7	1 30 30	2 -8 8	H ⁻¹⁰ K ^a 11	9 15 15	3 75 78	3 65 60	H ² K ^a 6	0 70 71	
8 18 14	7 35 34	7 25 25	H ⁻⁶ K ^a 8	1 -6 9	H ⁻¹⁰ K ^a 11	9 15 15	3 75 78	3 65 60	H ² K ^a 6	0 70 71	
7 42 45	5 74 74	6 47 44	H ⁻⁶ K ^a 8	1 -6 9	H ⁻¹⁰ K ^a 11	9 15 15	3 75 78	3 65 60	H ² K ^a 6	0 70 71	
6 28 26	4 113 117	5 26 26	7 13 10	1 -6 9	H ⁻¹⁰ K ^a 11	9 15 15	3 75 78	3 65 60	H ² K ^a 6	0 70 71	
5 29 26	2 267 214	3 34 34	5 21 22	1 -6 9	H ⁻¹⁰ K ^a 11	9 15 15	3 75 78	3 65 60	H ² K ^a 6	0 70 71	
4 84 83	1 377 423	2 78 81	4 -12 5	1 -6 9	H ⁻¹⁰ K ^a 11	9 15 15	3 75 78	3 65 60	H ² K ^a 6	0 70 71	
3 -5 15	2 118 113	H ⁻³ K ^a 12	1 77 83	3 68 67	H ⁻¹⁰ K ^a 11	9 15 15	3 75 78	3 65 60	H ² K ^a 6	0 70 71	
2 118 113	H ⁻³ K ^a 12	1 77 83	1 237 140	1 70 71	H ⁻¹⁰ K ^a 11	9 15 15	3 75 78	3 65 60	H ² K ^a 6	0 70 71	
1 186 192	3 11 12	H ⁻⁴ K ^a 6	1 70 71	0 194 274	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
H ⁻¹ K ^a 4	2 33 16	8 13 13	H ⁻⁶ K ^a 7	1 168 185	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
8 44 46	1 -7 8	7 42 44	7 -6 3	3 107 114	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
7 29 30	H ⁻³ K ^a 11	6 21 29	7 -6 3	4 210 198	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
6 54 53	4 -6 9	4 18 27	5 23 21	5 129 127	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
5 47 45	4 -6 9	3 10 27	3 128 136	6 25 24	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
4 117 116	1 41 42	1 62 73	2 42 40	7 76 75	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
3 291 285	2 15 17	1 15 10	H ⁻⁴ K ^a 5	8 16 14	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
2 160 162	1 51 52	H ⁻⁴ K ^a 5	1 15 10	9 16 14	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
1 268 245	H ⁻³ K ^a 10	8 43 46	H ⁻⁷ K ^a 13	1 255 258	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
H ⁻¹ K ^a 3	5 24 24	7 61 63	1 19 19	2 60 48	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
8 12 12	4 21 19	5 21 16	H ⁻⁷ K ^a 12	3 79 79	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
8 50 52	1 84 83	4 35 39	5 29 27	4 92 93	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
7 56 57	2 75 72	3 149 142	5 18 15	5 29 27	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
6 31 32	1 41 42	1 137 131	1 14 13	6 81 72	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
5 70 73	H ⁻³ K ^a 9	H ⁻⁵ K ^a 13	H ⁻⁷ K ^a 11	7 65 64	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
4 87 86	6 23 21	1 20 16	H ⁻⁷ K ^a 11	8 14 13	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
3 107 112	5 15 14	2 22 21	H ⁻⁷ K ^a 11	9 12 11	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
2 174 157	3 14 36	3 -5 1	H ⁻⁷ K ^a 11	10 13 10	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
1 387 402	2 15 14	H ⁻⁵ K ^a 12	3 -5 1	11 10 10	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
H ⁻¹ K ^a 2	1 159 160	1 13 15	H ⁻⁷ K ^a 10	12 10 10	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
9 16 16	2 19 16	3 17 16	H ⁻⁷ K ^a 10	13 10 10	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
8 16 19	7 37 37	H ⁻³ K ^a 11	H ⁻⁵ K ^a 11	14 10 10	H ⁻¹ K ^a 2	0 121 113	H ² K ^a 3	4 46 47	2 -12 18	0 35 34	
6 63 60	6 38 37	7 15 15	H ⁻⁵ K ^a 11	15 10 10	H ⁻¹ K ^a 2	0 121 113	H ²				

Table 7. Bond lengths (in Å) with estimated standard deviations in parentheses

C(1)—C(2)	1.561 (7)	C(2)—H(21)	1.09 (9)
C(1)—C(6)	1.498 (8)	C(3)—H(31)	1.17 (11)
C(1)—C(10)	1.522 (7)	C(3)—H(32)	1.09 (13)
C(1)—C(14)	1.544 (9)	C(4)—H(41)	1.08 (13)
C(2)—C(3)	1.519 (11)	C(4)—H(42)	1.00 (11)
C(2)—C(15)	1.555 (12)	C(5)—H(51)	0.92 (12)
C(3)—C(4)	1.499 (13)	C(5)—H(52)	0.96 (11)
C(4)—C(5)	1.487 (10)	C(7)—H(71)	0.90 (13)
C(5)—C(6)	1.520 (10)	C(9)—H(91)	0.83 (9)
C(6)—C(7)	1.346 (9)	C(10)—H(101)	0.74 (10)
C(7)—C(8)	1.446 (10)	C(13)—H(131)	0.94 (6)
C(8)—C(9)	1.439 (10)	C(13)—H(132)	0.95 (7)
C(8)—O(1)	1.226 (9)	C(13)—H(133)	0.89 (8)
C(9)—C(10)	1.506 (9)	C(14)—H(141)	1.05 (4)
C(9)—C(11)	1.536 (7)	C(14)—H(142)	0.92 (6)
C(10)—C(11)	1.501 (9)	C(14)—H(143)	0.96 (6)
C(11)—C(12)	1.519 (10)		
C(11)—C(13)	1.493 (10)		

Table 8. Valency angles (°) with estimated standard deviations in parentheses

C(2)—C(1)—C(6)	108.8 (5)	C(7)—C(8)—C(9)	118.0 (5)
C(2)—C(1)—C(10)	109.8 (3)	C(7)—C(8)—O(1)	121.3 (6)
C(2)—C(1)—C(14)	112.5 (4)	C(9)—C(8)—O(1)	120.7 (6)
C(6)—C(1)—C(10)	112.5 (4)	C(8)—C(9)—C(10)	118.7 (5)
C(6)—C(1)—C(14)	106.8 (4)	C(8)—C(9)—C(11)	120.4 (5)
C(10)—C(1)—C(14)	106.3 (5)	C(10)—C(9)—C(11)	59.1 (5)
C(1)—C(2)—C(3)	112.3 (4)	C(1)—C(10)—C(9)	121.3 (4)
C(1)—C(2)—C(15)	112.0 (6)	C(1)—C(10)—C(11)	126.7 (5)
C(3)—C(2)—C(15)	112.3 (6)	C(9)—C(10)—C(11)	61.4 (4)
C(2)—C(3)—C(4)	111.4 (6)	C(9)—C(11)—C(10)	59.5 (5)
C(3)—C(4)—C(5)	110.6 (7)	C(9)—C(11)—C(12)	118.4 (5)
C(4)—C(5)—C(6)	112.0 (5)	C(9)—C(11)—C(13)	115.3 (6)
C(1)—C(6)—C(5)	115.7 (4)	C(10)—C(11)—C(12)	123.5 (5)
C(1)—C(6)—C(7)	123.2 (5)	C(10)—C(11)—C(13)	115.0 (6)
C(5)—C(6)—C(7)	121.0 (5)	C(12)—C(11)—C(13)	114.3 (6)
C(6)—C(7)—C(8)	124.7 (5)		

Angles involving hydrogen atoms range from 98–130°.

adjacent ring carbon should bisect the three-membered ring; thus the carbonyl π -orbitals are parallel to the ring plane and symmetrically disposed with respect to the $2s-2p(\sigma)$ hybrid orbitals of the ring (Cornwell & Hudson, 1953; Ree & Martin, 1970). The carbonyl oxygen may be in either the *cis* or the *trans* configuration.

In the present structure the carbonyl plane (plane 2) makes an angle of 108.5° with the ring (plane 1), while the Newman projection (Fig. 3) down the C(8)—C(9) bond shows that the carbonyl oxygen deviates by 29.6° from the ideal *trans*-bisected orientation. Even with these deviations from ideal geometry the degree of conjugation is high, with the C(8)—C(9) distance of 1.439 (10) Å only slightly shorter than the single bond between the two $C(sp^2)$ atoms C(7) and C(8). This latter distance of 1.446 (10) Å is very close to the expected value (Sutton, 1965). It is noteworthy that the C(8)—C(9) bond is significantly shorter than the corresponding carbonyl-cyclopropane 'link bond' in cyclopropane carboxamide (Long, Maddox & Trueblood, 1969), cyclopropane carbohydrazide (Chesnut & March, 1958), and cyclopropane-1,1-dicarboxylic acid

Table 9. Details of mean planes in (-)-aristolone

The columns are: atom label, d , d/σ , where d is the perpendicular distance in Å of an atom from the plane, σ is the mean standard deviation of the atomic position obtained in the least-squares refinement. Atoms marked * were not included in mean-plane calculations.

Plane 1		Plane 3: double bond	
Cyclopropane ring: planar		C(1)	0.002 0.3
equation given below.		C(5)	0.009 1.3
		C(6)	-0.013 2.0
		C(7)	-0.005 0.7
		C(8)	-0.007 1.0
		O(1)*	0.173 —
		C(9)*	-0.153 —
Plane 2: carbonyl group		Plane 4: double bond/ carbonyl system	
C(7)	0.002 0.3	C(1)	0.098 14.0
C(8)	0.007 1.0	C(5)	-0.018 2.3
C(9)	0.002 0.3	C(6)	-0.009 1.3
O(1)	0.003 0.4	C(7)	-0.054 7.8
C(6)*	0.160 —	C(8)	-0.019 2.5
C(1)*	0.362 —	O(1)	0.095 13.6
C(5)*	0.189 —	C(9)	-0.093 13.2

Plane 5: ring B

C(1)	0.086	12.3
C(6)	-0.034	4.9
C(7)	-0.039	5.3
C(8)	0.056	8.1
C(9)	0.001	0.1
C(10)	-0.070	9.8
C(11)*	-1.279	—
O(1)*	0.204	—

Equations of planes, where X, Y, Z are coordinates in Å

- (1) $0.7366X - 0.6195Y + 0.2713Z - 5.6045 = 0$
- (2) $0.2210X + 0.9189Y + 0.3267Z - 5.5536 = 0$
- (3) $0.3322X + 0.9123Y + 0.2395Z - 6.7657 = 0$
- (4) $0.2753X + 0.9257Y + 0.2594Z - 6.1826 = 0$
- (5) $0.2616X + 0.9393Y + 0.2219Z - 5.9713 = 0$

Angles between planes

1-2	108.5°	2-4	5.0°
1-3	104.8	2-5	6.6
1-4	107.5	3-4	3.5
1-5	109.2	3-5	4.5
2-3	8.1	4-5	2.4

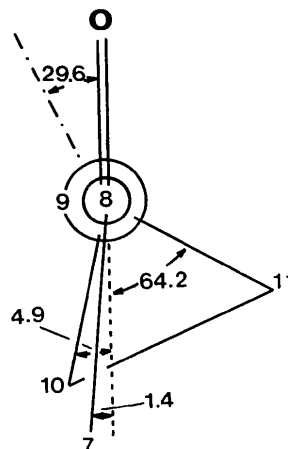


Fig. 3. Newman projection down the bond C(8)—C(9)

(Meester, Schenk & MacGillavry, 1971), the respective values are 1.487 (7), 1.48 (1), and 1.483 (5). The three examples cover both *cis* and *trans* configurations, and the maximum deviation of the carbonyl oxygen from the bisected position is 9°. However, in a recent paper (Luhan & McPhail, 1972) a distance of 1.456 (6) Å was reported for the cyclopropane-carbonyl link bond in *trans*-2,*trans*-3-dimethyl cyclopropane carboxylic acid, with the carbonyl oxygen 7.5° from the *cis*-bisected position. It is possible that the additional foreshortening of C(7)–C(8) in the present structure is due to the presence of the C(6)–C(7) double bond which is also conjugated with the carbonyl. This particular system is rare. It does occur however in 23(*R*)-23-hydroxy-3,5-cycloergost-7-en-6-one (Neidle & Hursthouse, 1972). The cyclopropane-carbonyl link bond is longer than might be expected from the above discussion at 1.463 (12) Å (carbonyl oxygen 19.1° from *cis*-bisected), but the degree of carbonyl-double bond conjugation is low, the C(*sp*²)–C(*sp*²) 'single bond' being 1.512 (10) Å.

The mean C(*sp*³)–C(*sp*³) distance is 1.522 (11) Å, and the mean C(*sp*³)–C(*sp*²) distance is 1.509 (9) Å, both close to their expected values. The mean bond length in the cyclopropane ring is 1.514 (9) Å, which is significantly shorter than the normal C(*sp*³)–C(*sp*³) value due to 'bent-bonding' (Coulson & Moffitt, 1949) which brings the atomic nuclei into closer proximity.

Fig. 2 shows that ring *A* adopts a slightly distorted

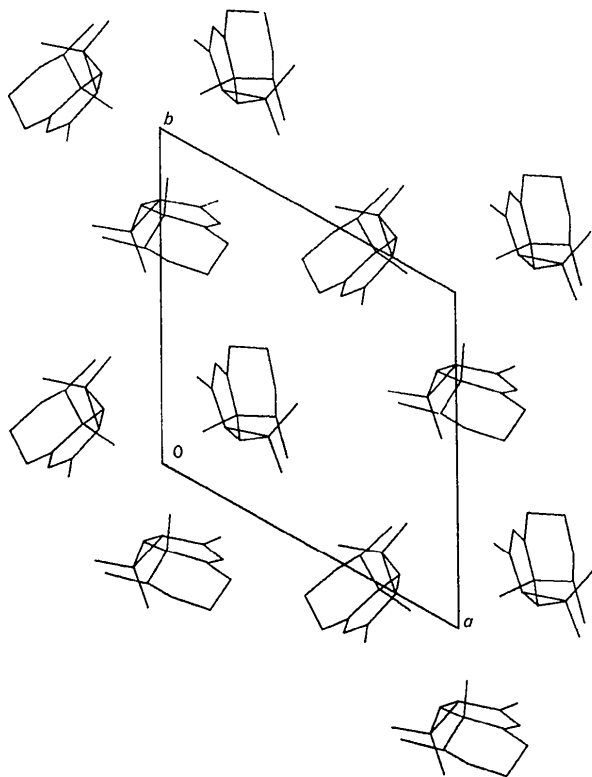


Fig. 4. Molecular packing projected down the *c* axis.

chair conformation with $|\omega|$ -values ranging from 49.0 to 57.9°. The mean value of 53.6 (8)° is a little lower than the value of 55.8° predicted from minimum-energy calculations by Bucourt & Hainaut (1965). A more useful comparison is afforded by noting that ring *A* in (–)-aristolone is somewhat analogous to the *B*-ring of steroids which contain the conjugated Δ^4 -en-3-one system. In two recent examples, 20(*S*)-hydroxyprogesterone (Isaacs, Motherwell, Coppola & Kennard, 1972*a*), and epitestosterone (Isaacs, Motherwell, Coppola & Kennard, 1972*b*) torsion angles in ring *B* ranged from 47.4 (5) to 57.2 (4)° and 47.4 (4) to 57.6 (4)° and averaged 52.7 and 52.5° respectively. Minimum-energy calculations on the system (Geise, Altona & Romers, 1967) indicate a spread of 43–62° with a mean of 52.3°.

Ring *B* in (–)-aristolone is, conversely, analogous to ring *A* in the steroids mentioned above, where the Δ^4 -en-3-one system forces the ring into a 'half-chair' conformation. The added presence of the three-membered ring in (–)-aristolone flattens ring *B* very considerably, so that none of the ring atoms deviates by more than 0.086 Å (12 σ) from the mean plane (plane 5, Table 9). The atoms of the conjugated carbonyl/double bond system are not, however, strictly coplanar (plane 4), and the extra-annular torsion angle C(6)–C(7)–C(8)–O(1) is 171.3 (7)°.

The molecular packing viewed along the 3₂-screw axis *c* is shown in Fig. 4. The mode of packing is governed by van der Waals interactions involving the methyl groups and the ring atoms C(4), C(5) and C(10). The shortest contacts are C...C 3.90, C...O 3.46, C...H 3.17, O...H 2.73 and H...H 2.42 Å.

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The Crystal Structure of 1,4-Dimethyl-5-ethyl-5-hydroxy- Δ^2 -1,2,3-triazoline

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1,4-Dimethyl-5-ethyl-5-hydroxy- Δ^2 -1,2,3-triazoline ($C_6H_{13}N_3O$) crystallizes in space group $P2_12_12_1$ (No. 19) with $a = 11.530$ (8), $b = 11.839$ (7), and $c = 5.862$ (3) Å, $Z = 4$. The structure was solved by direct methods and refined by the full-matrix least-squares method to an R of 0.050, using 1578 diffractometric X-ray intensities. Two symmetry-related reflexions were measured for each of the 841 independent reflexions. The triazoline ring adopts an envelope conformation with C(5) at the flap of the envelope. The alkyl groups are all equatorial whereas the hydroxy group is axial. The structure is held together by one intermolecular $OH \cdots N$ hydrogen bond and van der Waals forces.

Introduction

Nuclear magnetic resonance studies (Olsen, 1969) on 5-hydroxy- and 5-amino-triazolines have directed interest towards conformation studies of the five-membered ring system triazoline. A deshielding effect was observed on substituents at C(4) situated *cis* with respect to a nitrogen or oxygen atom attached to C(5). This effect could arise from an interaction of the C(4) substituent with the lone pair of the heteroatom at C(5), but it might also be ascribed to an envelope-like conformation of the triazoline ring system (Olsen, 1969). This X-ray crystallographic investigation was undertaken in order to distinguish between these two possibilities, and the result supports the latter interpretation. A series of structure determinations is now

being planned in cooperation with C. E. Olsen, Department of Organic Chemistry, The Royal Veterinary and Agricultural University, Copenhagen, in order to investigate the conformation of the triazoline ring as a function of different substituents.

Experimental

1,4-Dimethyl-5-ethyl-5-hydroxy- Δ^2 -1,2,3-triazoline was prepared (Olsen, 1969) and crystallized for data collection by C. E. Olsen. Colourless orthorhombic crystals elongated along the c axis were formed from an ether solution. Weissenberg and precession photographs showed that $h00$ were absent for $h \neq 2n$, $0k0$ for $k \neq 2n$, and $00l$ for $l \neq 2n$, so the space group was $P2_12_12_1$ (No. 19). The compound had been prepared as a racemate.