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The Structures of Two Derivatives of Bicyclo[3,3,1]nonane-2,4,9-trione. A Natural Product: Clusianone, $C_{33}H_{42}O_4$, and Trimethylated Catechinic Acid, $C_{18}H_{20}O_6$

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The structures of two derivatives of bicyclo[3,3,1]nonane-2,4,9-trione were solved by direct methods. The structures of clusianone, $C_{33}H_{42}O_4$, and trimethylated catechinic acid, $C_{18}H_{20}O_6$, were refined by standard least-squares techniques to weighted $R(F)$ values of 0·038 and 0·046 respectively using diffractometer data. The two molecules are compared and unusually long $C(sp^3)$–$C(sp^3)$ bonds are discussed. Clusianone contains a 1·603 (4) Å carbon–carbon bond.

Introduction

As a consequence of two originally unrelated investigations, we found ourselves with two structures each containing the unusual bicyclo[3,3,1]nonane-2,4,9-trione ring system. Because of their similarity and to facilitate comparisons, we are describing them together.

(I) $C_{33}H_{42}O_4$–*clusianone*

As part of a study of the resinous products of the plants of the family *Guttiferae*, a sample of *Clusia congestiflora* collected near Fresno, Colombia, was examined. Extraction of bark and broken twigs with hexane yielded clusianone (I) as a yellow crystalline material (m.p. 150–152°C). Combustion and mass spectral analyses showed the formula to be $C_{33}H_{42}O_4$ and indicated the probable presence of a benzoyl group. Although various structural features were recognized on spectroscopic grounds, no definitive structure could be advanced on the basis of chemical evidence and recourse was had to crystallographic methods.

(II) $C_{18}H_{20}O_6$–*trimethylcatechinic acid*

Treatment of the natural polyphenolic polymer of conifer bark with base leads to 'bark phenolic acids'. In studies directed toward understanding this change, the model compound catechin was found to be similarly transformed by mild alkali into 'catechinic acid' (Sears, Casebier, Hergert, Stout & McCandlish, 1974). As a result of the complexity of the transformation an X-ray structure determination on crystalline (m.p. 193–194°C) trimethylated catechinic acid (II) was undertaken.

Experimental

Data for each crystal were collected on a Picker diffractometer equipped with a pulse-height analyzer and using Nb-filtered Mo $K\alpha$ radiation. Cell constants were obtained by least-squares refinement of selected 2θ values. Experimental conditions and crystal data are summarized in Table 1. Standard reflections were measured periodically during data collection to obtain a scale factor for each data group. The data were corrected for background, coincidence loss and the usual Lorentz and polarization effects.

Table 1. *Room-temperature experimental data*

	$C_{33}H_{42}O_4$	$C_{18}H_{20}O_6$
Space group	$Pna2_1$	$P2_12_12_1$
Z	4	4
Cell constants	$a=15{\cdot}291$ (3)* Å $b=19{\cdot}725$ (3) $c=9{\cdot}487$ (2)	$a=16{\cdot}703$ (9) Å $b=13{\cdot}286$ (7) $c=7{\cdot}320$ (3)
Number of 2θ values refined	12	14
Density	$\varrho_c=1{\cdot}167$ g cm^{-3} $\varrho_m=1{\cdot}15$	$\varrho_c=1{\cdot}368$ g cm^{-3}
Linear absorption coefficient		
$\mu_{\text{Mo }K\alpha}$	0·808 cm^{-1}	1·105 cm^{-1}
μr_{max}	$6{\cdot}0\times10^{-2}$	$7{\cdot}7\times10^{-2}$
Number of reflections	4398	1639
2θ max	60°	50°
Scan range (deg.)	$1+\tan\theta$	$2{\cdot}4+\tan\theta$
Scan speed	2° min^{-1}	2° min^{-1}
Backgrounds	2 × 10 s, $0<2\theta<35°$; 2 × 20 s, $35°<2\theta<60°$	2 × 10 s
Standard reflections	3	6
Data group scale factors	1·0	0·98–1·02
Unobserved cut off	$2\sigma_{Fo}$	$3\sigma_{Fo}$
Observed reflections	3446	1060

* Standard deviations in terms of the least significant figure are given in parentheses throughout this paper.

(I) Single crystals of clusianone in the form of elongated prisms were grown by evaporation from a 95% ethanol solution. Precession photographs showed orthorhombic symmetry with systematic absences ($0kl$ with $k+l\neq2n$ and $h0l$ with $h\neq2n$) consistent with the space groups $Pnam$ and $Pna2_1$. The non-centrosymmetric polar group $Pna2_1$ was favored on the basis of a measured density requiring four molecules per unit cell and the existence of spectroscopic data inconsistent with a molecule having the symmetry of the special positions in *Pnam*.

Earlier attempts at solving the structure from limited Cu $K\alpha$ data by both direct methods and Patterson search methods had been unsuccessful. As a result extra care was taken to ensure that collection of the current extended data set yielded accurate intensities, especially for reflections having $2\theta_{\mathrm{Mo}\,K\alpha}$ values greater than 45°. Of the reflections in this group, the 177 having the highest measured intensities were collected twice and the results averaged to improve their precision. The standards gave no indication of systematic decomposition of the crystal; so all reflection data were accepted as being on a single scale.

(II) Single crystals of (II) were grown by evaporation from benzene. Weissenberg photographs showed orthorhombic symmetry with systematic absences ($h00$ with $h \neq 2n$; $0k0$ with $k \neq 2n$; $00l$ with $l \neq 2n$) uniquely consistent with space group $P2_12_12_1$. The crystals were not of sufficient quality to obtain an accurate experimental density.

Three-dimensional data collection required a large scan width since the best crystals obtainable gave wide, highly structured peaks. The standard reflections gave an experimental instability constant of 0·6 % (McCandlish, Stout & Andrews, 1975). This, as well as estimated errors in the coincidence loss parameter ($\sigma = 0{\cdot}4 \times 10^{-8}$) and the scale factor ($\sigma = 1{\cdot}2 \times 10^{-2}$), was included in the calculated standard deviation of the intensity of each reflection.

Solution and refinement of the structures

Both structures were solved by use of *MULTAN* (Germain, Main & Woolfson, 1971), although in both cases extended starting phase sets were required and a large number of final phase sets were developed. In the case of (II), an early failure in a key $\sum_2$ relationship led to difficulties (see below). The basic parameters for the solutions are given in Table 2. In the phase refinements the phases of the starting set reflections were held constant until the tangent formula refinement had converged. They were then allowed to refine to their final values.

Table 2. *Solution parameters*

	(I)	(II)
Overall B	3·09 Å^2	3·88 Å^2
Min. E used	1·70	1·50
E's > min	283	188
$\sum_2$ relationships used	2000	1500
Number of starting reflections	6	8
Number of phase sets	32	64

(I) In addition to the three origin/enantiomorph determining reflections found by the program, three other reflections were found to have $\alpha_{\mathrm{EST}} < 1{\cdot}16$ and were included with phases as in Table 3 in generating the 32 starting sets. Each of these was developed into a complete phase set for the 283 reflections using a weighted tangent formula refinement (Germain, Main & Woolfson, 1971) and the 2000 strongest $\sum_2$ relations. Of the 32 starting phase sets, 27 produced final sets having weighted residuals, R_k, between 32·5% and 36·2%. One other set had a residual of 28·6%, while the remaining 4 sets had residuals between 27·2% and 27·4%. An E map using weighted E's as the Fourier coefficients was calculated for the set of 283 phases having the smallest residual. The interpeak distances of the 50 highest peaks in this map were examined and a chemically reasonable connectivity pattern of 28 atoms was found. An F_o Fourier map with phases based on the 28 atom model revealed the locations of the remaining 9 non-hydrogen atoms in the molecule. The resulting 37 atom model gave an initial value of $R(F) = 0{\cdot}256$ using 2139 reflections with $\sin\theta/\lambda < 0{\cdot}55$.

Table 3. *Starting set of reflections, their E's and their assigned phases for clusianone*

h	k	l	E	φ
1	12	12	3·58	45°
6	3	1	2·39	0
14	1	0	3·77	0
7	13	3	2·24	±45, ±135
6	1	7	2·21	±45, ±135
5	20	0	2·66	0, 180

The initial model was refined using standard least-squares techniques (Stewart, Kruger, Ammon, Dickinson & Hall, 1972). Carbon and oxygen scattering factors were those of Doyle & Turner (1968). Scattering factors for hydrogen were from Stewart, Davidson & Simpson (1965). The anomalous dispersion effect was ignored. The quantity minimized was $\sum w(|F_o| - |F_c|)^2$. Unit weights were used through the first two cycles of anisotropic refinement and statistical weights defined as $1/\sigma^2_{Fo}$ were used thereafter. Full-matrix isotropic least-squares refinement of the 37 atom model converged to $R(F) = 0{\cdot}115$. Two anisotropic cycles of least-squares refinement resulted in an $R(F) = 0{\cdot}085$. The matrix was partitioned into two non-overlapping blocks along its diagonal. 32 of 42 hydrogen atoms were found using ΔF Fourier syntheses. The 10 methyl hydrogens not located from ΔF maps were placed at calculated positions. With all atoms included, the 79 atom model resulted in an $R(F) = 0{\cdot}064$. At this point a reflection was given zero weight if its F_o was less than $2\sigma_{Fo}$. Such 'less than' reflections were allowed to contribute to the refinement when $F_c > 2\sigma_{Fo}$. In addition all reflections outside the range $0{\cdot}15 < \sin\theta/\lambda < 0{\cdot}75$ were arbitrarily eliminated. It has been observed in this laboratory that if reflections with small $\sin\theta/\lambda$ are not collected by hand their intensities are unreliable. Furthermore these reflections are the ones which tend to suffer most from extinction effects. Of the 4347 reflections in the range considered, 901 were calculated

Table 4. C *and* O *parameters and their least-squares standard deviations for clusianone*

The temperature factor coefficients are defined by:

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

	x ($\times 10^5$)	y ($\times 10^5$)	z ($\times 10^4$)	U_{11} ($\times 10^4$)	U_{22} ($\times 10^4$)	U_{33} ($\times 10^4$)	U_{12} ($\times 10^4$)	U_{13} ($\times 10^4$)	U_{23} ($\times 10^4$)
C(1)	21223 (17)	22519 (12)	4204 (3)	355 (14)	301 (12)	359 (14)	−36 (11)	30 (12)	17 (11)
C(2)	26286 (17)	26191 (12)	5338 (3)	379 (14)	332 (12)	321 (13)	41 (11)	17 (12)	20 (11)
C(3)	31001 (17)	32098 (13)	5102	381 (14)	361 (13)	321 (14)	−41 (11)	−2 (12)	7 (11)
C(4)	33401 (18)	33665 (12)	3628 (3)	431 (15)	279 (12)	390 (14)	12 (12)	56 (13)	10 (12)
C(5)	28111 (17)	30473 (12)	2416 (3)	415 (14)	317 (12)	319 (13)	−2 (11)	7 (13)	58 (11)
C(6)	33536 (18)	24391 (13)	1716 (3)	492 (15)	346 (13)	300 (12)	7 (12)	30 (13)	25 (11)
C(7)	35227 (18)	18892 (12)	2863 (3)	455 (15)	337 (12)	331 (13)	10 (12)	36 (12)	33 (11)
C(8)	26918 (17)	16642 (12)	3612 (3)	505 (16)	297 (12)	388 (14)	1 (12)	36 (14)	74 (12)
C(9)	19827 (19)	27278 (13)	2981 (3)	457 (16)	323 (13)	352 (14)	6 (11)	−28 (13)	−17 (11)
C(10)	34239 (19)	35783 (14)	6314 (3)	452 (17)	473 (16)	419 (16)	−44 (13)	0 (15)	−46 (15)
C(11)	37263 (19)	42961 (14)	6304 (4)	454 (17)	440 (16)	501 (18)	−60 (13)	71 (15)	−82 (15)
C(12)	34225 (22)	47604 (15)	5348 (4)	712 (23)	446 (17)	556 (19)	−50 (16)	51 (18)	−105 (16)
C(13)	36819 (28)	54376 (17)	5455 (5)	1084 (32)	429 (18)	773 (26)	−82 (19)	139 (26)	−83 (20)
C(14)	42483 (29)	56342 (19)	6501 (6)	903 (30)	550 (21)	987 (33)	−209 (21)	238 (28)	−255 (24)
C(15)	45380 (24)	51727 (22)	7454 (5)	711 (26)	783 (26)	939 (21)	−229 (22)	−24 (25)	−294 (26)
C(16)	42705 (22)	45023 (18)	7397 (4)	624 (21)	619 (20)	799 (26)	−88 (18)	−136 (21)	−179 (20)
C(17)	42303 (20)	26921 (14)	1141 (3)	628 (20)	467 (16)	504 (18)	15 (14)	212 (16)	63 (15)
C(18)	28239 (23)	21419 (14)	479 (3)	828 (24)	486 (17)	355 (15)	14 (16)	−44 (17)	−19 (15)
C(19)	25848 (20)	36180 (14)	1355 (3)	608 (19)	439 (15)	392 (16)	59 (14)	62 (15)	144 (14)
C(20)	21516 (21)	42188 (16)	2008 (3)	622 (20)	541 (18)	489 (19)	156 (16)	23 (16)	173 (15)
C(21)	24097 (23)	48597 (16)	1899 (4)	694 (23)	461 (17)	745 (25)	150 (17)	−80 (20)	123 (17)
C(22)	32103 (27)	50843 (16)	1169 (5)	858 (27)	509 (20)	1390 (40)	−18 (19)	125 (29)	284 (26)
C(23)	18686 (28)	54246 (18)	2543 (6)	1115 (33)	575 (21)	1226 (35)	351 (22)	−92 (31)	−2 (25)
C(24)	40008 (21)	12535 (15)	2271 (3)	694 (20)	467 (16)	444 (17)	149 (15)	180 (16)	0 (14)
C(25)	44008 (20)	8194 (15)	3410 (4)	569 (19)	475 (15)	498 (18)	139 (15)	27 (16)	−47 (15)
C(26)	42152 (21)	1834 (15)	3704 (4)	531 (18)	498 (16)	550 (20)	162 (15)	96 (17)	60 (16)
C(27)	35189 (26)	−2250 (17)	3009 (4)	851 (27)	619 (22)	1031 (33)	−79 (20)	−86 (26)	115 (23)
C(28)	47213 (25)	−1935 (18)	4831 (5)	949 (31)	694 (25)	788 (27)	233 (22)	6 (25)	214 (22)
C(29)	12525 (18)	19699 (14)	4807 (3)	425 (16)	371 (14)	478 (17)	−65 (12)	77 (14)	25 (13)
C(30)	6805 (18)	25064 (14)	5463 (4)	373 (15)	463 (16)	578 (18)	29 (13)	50 (15)	67 (16)
C(31)	4475 (19)	25657 (16)	6791 (4)	416 (16)	491 (17)	636 (20)	−45 (14)	105 (16)	−38 (16)
C(32)	7212 (25)	20979 (19)	7962 (4)	747 (25)	953 (28)	649 (25)	125 (22)	230 (21)	154 (22)
C(33)	−1366 (23)	31375 (18)	7252 (5)	683 (23)	733 (24)	991 (30)	51 (20)	322 (23)	−137 (23)
O(2)	25892 (13)	23409 (9)	6583 (2)	572 (12)	534 (12)	380 (11)	−85 (10)	−19 (10)	132 (10)
O(4)	39645 (13)	37345 (9)	3345 (2)	588 (12)	447 (12)	535 (13)	−196 (9)	129 (11)	−21 (10)
O(9)	12763 (13)	28027 (11)	2431 (2)	471 (12)	726 (14)	558 (13)	−48 (10)	−136 (11)	174 (12)
O(10)	34004 (15)	32938 (11)	7510 (2)	852 (16)	653 (14)	364 (11)	−181 (13)	−90 (12)	6 (11)

as 'less thans'. Least-squares refinement (three non-overlapping blocks) of the complete model in the mixed temperature factor mode (isotropic H's) converged to an $R(F)=0{\cdot}038$ for the 3446 observed reflections. At convergence the calculated shift was less than σ for all carbon and oxygen parameters, and the standard deviation of an observation of unit weight was 1·35. The final atomic coordinates and thermal parameters are given in Tables 4 and 5.*

(II) Initially the first six reflections in Table 6 were used to generate starting points. Sixteen different sets of phases for the 188 reflections having $E > 1{\cdot}5$ were developed using the weighted tangent formula and the 1500 $\sum_2$ relations previously derived. The four phase sets having the four lowest residuals ($31{\cdot}1 < R_K < 32{\cdot}3$) were used to calculate weighted E maps. These E maps gave no indication of a chemically reasonable structure.

Table 5. H *parameters and their least-squares standard deviations for clusianone*

The temperature factor coefficient is defined by

$$T=\exp\,\{-2\pi^2U[2\sin(\theta)/\lambda]^2\}\,.$$

	x($\times 10^4$)	y($\times 10^4$)	z($\times 10^4$)	U($\times 10^3$)
H(O2)	2970 (24)	2699 (16)	7440 (45)	152 (14)
H(71)	3956 (13)	2100 (10)	3478 (23)	29 (6)
H(81)	2845 (14)	1368 (11)	4371 (24)	31 (6)
H(82)	2272 (16)	1385 (12)	3007 (27)	55 (8)
H(121)	3061 (20)	4627 (14)	4457 (29)	90 (10)
H(131)	3616 (18)	5814 (14)	4653 (30)	104 (10)
H(141)	4392 (18)	6139 (14)	6447 (33)	93 (9)
H(151)	4892 (18)	5346 (13)	8328 (35)	105 (10)
H(161)	4582 (22)	4151 (18)	8075 (40)	120 (14)
H(171)	4146 (18)	3093 (14)	548 (33)	82 (9)
H(172)	4623 (21)	2845 (16)	1957 (37)	103 (12)
H(173)	4542 (18)	2328 (15)	593 (33)	87 (10)
H(181)	3120 (19)	1768 (14)	25 (34)	73 (9)
H(182)	2645 (21)	2464 (18)	−201 (33)	86 (11)
H(183)	2181 (23)	1972 (18)	733 (39)	107 (12)
H(191)	2209 (19)	3418 (13)	632 (30)	71 (9)
H(192)	3136 (19)	3685 (13)	924 (30)	66 (10)
H(201)	1581 (17)	4115 (12)	2539 (31)	72 (8)
H(221)	3563 (21)	4760 (18)	731 (38)	112 (12)
H(222)	3130 (24)	5452 (20)	440 (51)	146 (14)
H(223)	3563 (27)	5382 (24)	1765 (53)	178 (18)
H(231)	1610 (24)	5723 (18)	1909 (46)	122 (13)

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31542 (29 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 5 (*cont.*)

H(232)	1400 (26)	5234 (20)	3260 (49)	149 (15)
H(233)	2298 (27)	5741 (19)	3047 (45)	155 (15)
H(241)	3511 (16)	976 (12)	1670 (28)	54 (8)
H(242)	4443 (18)	1413 (13)	1586 (30)	80 (9)
H(251)	4904 (19)	1074 (16)	4019 (33)	89 (11)
H(271)	3133 (23)	41 (18)	2601 (41)	122 (13)
H(272)	3785 (23)	−578 (19)	2428 (42)	129 (13)
H(273)	3205 (27)	−492 (22)	3675 (58)	162 (15)
H(281)	5223 (18)	114 (15)	5290 (35)	81 (10)
H(282)	4225 (26)	−429 (19)	5518 (47)	158 (15)
H(283)	5067 (22)	−603 (17)	4390 (37)	109 (12)
H(291)	1365 (16)	1611 (12)	5514 (30)	58 (8)
H(292)	942 (17)	1761 (13)	3950 (32)	67 (9)
H(301)	475 (18)	2808 (13)	4748 (27)	64 (8)
H(321)	186 (21)	1942 (14)	8574 (33)	84 (9)
H(322)	1080 (19)	1758 (16)	7683 (33)	86 (10)
H(323)	993 (28)	2402 (25)	8575 (54)	180 (16)
H(331)	−234 (24)	3439 (18)	6418 (45)	138 (13)
H(332)	−636 (23)	2974 (16)	7867 (36)	110 (11)
H(333)	235 (22)	3369 (15)	7961 (35)	100 (11)

Table 6. *Starting set of reflections, their E's and their assigned phases for trimethylated catechinic acid*

h	k	l	E	φ
13	0	2	2·98	0°
0	8	3	2·90	0
0	5	4	2·31	90
5	10	3	2·17	45, 735
0	6	6	3·14	0, 180
7	12	4	2·21	±45, ±135
0	1	2	2·57	90, 270
0	7	5	2·22	90, 270

At this point we assumed that the phase expansion was unsuccessful due to a $\sum_2$ relation with $\varphi \neq 0$. We reasoned that for such a relation to be fatal it would have to appear in the initial steps of phase expansion (*i.e.* before reaching the point where phases are generated using multiple indications). Also it is likely to be associated with a reflection having a small α_{EST}. The convergence map revealed two likely suspects: 012 with $\alpha_{EST} = 3·23$ and 075 with $\alpha_{EST} = 2·81$. These two reflections were added to our starting list and 48 new phase sets developed. A weighted E map based on the phase set having the lowest residual ($R_K = 20·1$) yielded the structure. The single $\sum_2$ relation responsible for the phase of 012 had been 180° in error.

Of the 24 non-hydrogen atoms in the molecule, only one methyl carbon atom was not evident in the E map. An F_o Fourier map with phases based on the 23 atom model revealed its location. The resulting 24 atom model gave an initial $R(F) = 0·249$ using 1060 reflections having $F_o \geq 3\sigma_{F_o}$. The initial model was refined using standard least-squares techniques and scattering factors as described above. Unit weights were used for the first 4 cycles of refinement and $1/\sigma^2_{F_o}$ weights were used thereafter. Full-matrix refinement with isotropic temperature parameters for the initial 24 atom model converged after 4 cycles to an $R(F) = 0·107$. One cycle of full-matrix refinement with anisotropic temperature parameters reduced $R(F)$ to 0·081. The locations of 10 of the 20 hydrogen atoms in the molecule were found by using ΔF Fourier syntheses. Nine methyl hydrogen atoms and the hydrogen atom on O(7) were not located. The positions of six of the nine methyl hydrogen atoms were calculated assuming they were in the 'staggered' conformation. The three hydrogen atoms on C(17) and the one hydrogen atom on O(7) were never located. After partitioning the matrix into

Table 7. C *and* O *parameters and least-squares standard deviations for trimethylated catechinic acid*

The temperature factor coefficients are defined by:

$$T = \exp\left[-2\pi^2(h^2a^{*2}U_{11} + k^2b^{*2}U_{22} + l^2c^{*2}U_{33} + 2hka^*b^*U_{12} + 2hla^*c^*U_{13} + 2klb^*c^*U_{23})\right].$$

	x ($\times 10^4$)	y ($\times 10^4$)	z ($\times 10^4$)	U_{11} ($\times 10^3$)	U_{22} ($\times 10^3$)	U_{33} ($\times 10^3$)	U_{12} ($\times 10^3$)	U_{13} ($\times 10^3$)	U_{23} ($\times 10^3$)
C(1)	2419 (3)	7849 (4)	2294 (7)	63 (4)	36 (3)	31 (3)	−3 (3)	−3 (3)	5 (3)
C(2)	3028 (3)	8600 (4)	1700 (6)	46 (3)	48 (3)	27 (3)	−2 (3)	−5 (3)	−1 (3)
C(3)	2843 (4)	9567 (4)	1234 (7)	52 (4)	9 (3)	37 (3)	−6 (3)	0 (3)	1 (3)
C(4)	2023 (3)	9918 (4)	1286 (6)	55 (4)	47 (3)	32 (3)	0 (3)	−1 (3)	1 (3)
C(5)	1380 (3)	9167 (4)	1824 (7)	55 (4)	39 (3)	39 (3)	0 (3)	5 (3)	−1 (3)
C(6)	1064 (4)	8567 (4)	152 (8)	57 (4)	54 (4)	44 (3)	9 (4)	−8 (3)	7 (3)
C(7)	1681 (4)	7875 (4)	−746 (7)	60 (4)	40 (3)	31 (3)	−9 (3)	−3 (3)	4 (3)
C(8)	2098 (3)	7204 (4)	660 (7)	54 (4)	40 (3)	35 (3)	−6 (3)	8 (3)	−2 (3)
C(9)	1720 (3)	8400 (4)	3085 (7)	56 (4)	40 (3)	35 (3)	−14 (3)	1 (3)	−7 (3)
C(10)	2732 (3)	6510 (4)	−94 (7)	54 (3)	39 (3)	34 (3)	−9 (3)	2 (3)	3 (3)
C(11)	2857 (4)	5586 (4)	741 (8)	65 (4)	46 (4)	42 (3)	1 (3)	14 (3)	10 (3)
C(12)	3471 (4)	4949 (5)	207 (8)	74 (4)	48 (4)	52 (4)	6 (4)	3 (4)	6 (4)
C(13)	3975 (3)	5233 (4)	−1206 (7)	44 (3)	48 (3)	42 (3)	−6 (3)	3 (3)	0 (3)
C(14)	3848 (4)	6150 (4)	−2071 (7)	54 (4)	47 (3)	45 (3)	−15 (3)	−2 (3)	4 (3)
C(15)	3239 (4)	6782 (4)	−1497 (8)	62 (4)	41 (3)	47 (4)	−3 (3)	0 (3)	14 (3)
C(16)	4837 (5)	3788 (5)	−863 (12)	83 (6)	41 (4)	104 (6)	−8 (4)	−16 (5)	18 (4)
C(17)	4205 (5)	6160 (7)	−5175 (9)	112 (6)	202 (9)	36 (4)	−17 (6)	13 (4)	3 (5)
C(18)	4424 (5)	8799 (7)	1011 (12)	44 (4)	99 (6)	84 (6)	−5 (4)	7 (4)	4 (5)
O(2)	3764 (2)	8214 (3)	1712 (4)	50 (2)	63 (2)	50 (2)	9 (2)	−8 (2)	−7 (2)
O(4)	1845 (2)	10793 (2)	918 (5)	76 (3)	42 (2)	80 (3)	8 (2)	4 (2)	15 (2)
O(7)	1284 (2)	7260 (3)	−2042 (4)	80 (3)	56 (2)	41 (2)	−17 (2)	−12 (2)	−7 (2)
O(9)	1428 (2)	8213 (3)	4588 (5)	78 (3)	66 (3)	37 (2)	−19 (2)	7 (2)	3 (2)
O(13)	4596 (2)	4665 (3)	−1840 (5)	69 (3)	60 (2)	69 (2)	10 (2)	8 (2)	16 (2)
O(14)	4373 (3)	6461 (3)	−3410 (6)	74 (3)	81 (3)	74 (3)	−10 (2)	32 (3)	13 (3)

two non-overlapping blocks along the diagonal, six cycles of least-squares refinement based on the 40 atom model using anisotropic temperature factors for the heavy atoms and isotropic temperature factors for the hydrogen atoms converged to a weighted $R(F)=0{\cdot}046$ using the 1060 observed reflections. The final standard deviation in an observation of unit weight was 2·61, while the quantity (calculated shift/estimated error) was less than 1·0 for all heavy-atom parameters. The final atomic coordinates and thermal parameters are given in Tables 7 and 8.*

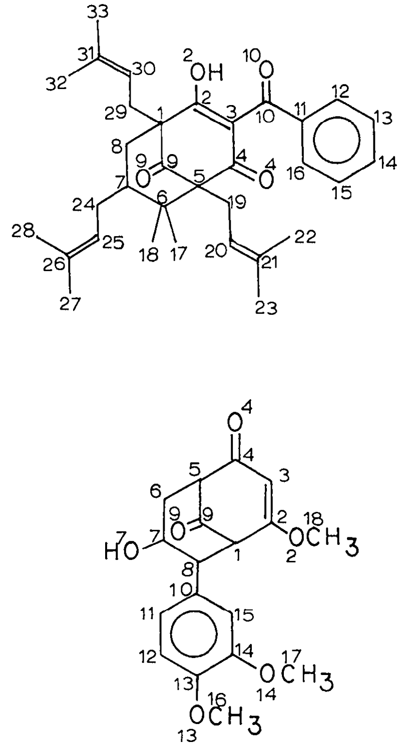

Fig. 1. Structures of clusianone and trimethylated catechinic acid.

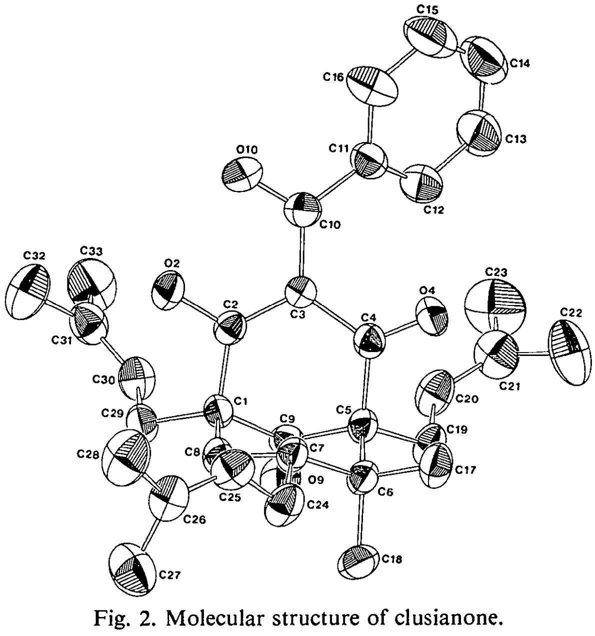

Fig. 2. Molecular structure of clusianone.

Table 8. H *parameters and least-squares standard deviations for trimethylated catechinic acid*

The temperature factor coefficient is defined by
$T=\exp\{-2\pi^2U[2\sin(\theta)/\lambda]^2\}$.

	$x(\times 10^3)$	$y(\times 10^3)$	$z(\times 10^3)$	$U(\times 10^3)$
H(1)	269 (3)	736 (4)	312 (7)	61 (15)
H(3)	320 (3)	1012 (4)	72 (7)	90 (19)
H(5)	88 (2)	946 (3)	233 (5)	33 (12)
H(61)	56 (3)	811 (3)	40 (7)	60 (16)
H(62)	88 (3)	900 (3)	−75 (6)	51 (15)
H(7)	216 (3)	827 (3)	−126 (6)	41 (13)
H(8)	167 (2)	681 (3)	106 (5)	19 (11)
H(11)	248 (3)	537 (4)	163 (8)	69 (19)
H(12)	352 (3)	427 (4)	81 (7)	67 (17)
H(15)	311 (3)	735 (3)	−202 (6)	30 (14)
H(161)	526 (6)	409 (7)	−7 (4)	216 (48)
H(162)	448 (3)	335 (4)	−98 (7)	47 (21)
H(163)	550 (8)	298 (8)	−106 (6)	393 (62)
H(181)	428 (4)	892 (5)	−6 (10)	73 (30)
H(182)	439 (5)	952 (6)	149 (10)	56 (35)
H(183)	513 (5)	841 (5)	95 (9)	163 (34)

Discussion

The chemical structures deduced for (I) and (II) are shown in Fig. 1. The structure finally obtained for (I) is a striking one from a chemical point of view. It is entirely consistent with other evidence, however, and although unique in detail, is reasonable in its biosynthetic relationship to other products of the same plant family (Karanjgoakar, Rama Rao, Venkataraman, Yemul & Palmer, 1973). The structure of (II) confirms that deduced from chemical data and spectra. The striking structural similarity of (I) and (II) is interesting in view of their totally different origins.

An *ORTEP* (Johnson, 1965) drawing of (I) is shown in Fig. 2. A crystal packing diagram viewed down the *c* axis is shown in Fig. 3. Bond lengths and bond angles are tabulated in Tables 9 and 10. An *ORTEP* drawing of (II) and a packing diagram are shown in Figs. 4 and 5 respectively. Bond lengths and bond angles are in Tables 11 and 12.

Aside from the gross structures, the most interesting feature of these molecules is the enolized triketo [3,3,1]bicyclononane system. Although the two molecules are similar, the additional benzoyl group of (I) produces some significant changes. Comparison of the observed bond lengths with normal values indicates that (I) can be represented as a resonance hybrid of the structures shown in Fig. 6. The relative unimportance of the third contributor is shown by a twist of 23° about the C(3)–C(4) bond, in contrast to the planarity of the system involving O(2) and O(10). Part

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* See previous footnote.

of the stabilization of *B* undoubtedly derives from the strong intramolecular hydrogen bond which exists in this molecule. H(O2) bridges O(2) and O(10), which are separated by 2·417 (3) Å. The hydrogen is located 1·22 (4) Å from O(2) and 1·35 (4) Å from O(10). The O(2)-H(O2)-O(10) bond angle is 140 (3)°. It is extremely likely that the asymmetrical nature of the hydrogen bridge is real in view of the systematic alternation of the bond lengths in the ring O(2)-C(2)-C(3)-C(10)-O(10)-H(O2).

The phenyl group does not appear to interact with the conjugated system in (I). The C(10)-C(11) distance is essentially an sp^2-sp^2 single bond length, and the twist angle about it is 32°, analogous to biphenyl at 42° (Bastiansen & Trætteberg, 1962).

(II) can only be a resonance hybrid of the structures shown in Fig. 7, and, as might have been expected in the absence of stabilization by hydrogen bonding, appears to show less electron delocalization.

Table 9. *Interatomic distances* (Å) *and their estimated standard deviations for clusianone*

C(1)—C(2)	1·511 (4)	C(11)–C(12)	1·370 (5)
C(1)—C(8)	1·555 (4)	C(11)–C(16)	1·390 (5)
C(1)—C(9)	1·507 (4)	C(12)–C(13)	1·397 (5)
C(1)—C(29)	1·551 (4)	C(13)–C(14)	1·373 (6)
C(2)—C(3)	1·388 (4)	C(14)–C(15)	1·371 (6)
C(2)—O(2)	1·303 (3)	C(15)–C(16)	1·386 (6)
C(3)—C(4)	1·478 (3)	C(19)–C(20)	1·492 (4)
C(3)—C(10)	1·447 (3)	C(20)–C(21)	1·328 (5)
C(4)—C(5)	1·541 (4)	C(21)–C(22)	1·475 (6)
C(4)—O(4)	1·229 (3)	C(21)–C(23)	1·516 (5)
C(5)—C(6)	1·603 (4)	C(24)–C(25)	1·508 (4)
C(5)—C(9)	1·513 (4)	C(25)–C(26)	1·316 (4)
C(5)—C(19)	1·549 (4)	C(26)–C(27)	1·489 (5)
C(6)—C(7)	1·559 (4)	C(26)–C(28)	1·515 (5)
C(6)—C(17)	1·531 (4)	C(29)–C(30)	1·507 (4)
C(6)—C(18)	1·542 (4)	C(30)–C(31)	1·315 (5)
C(7)—C(8)	1·522 (4)	C(31)–C(32)	1·504 (5)
C(7)—C(24)	1·556 (4)	C(31)–C(33)	1·503 (5)
C(9)—O(9)	1·209 (4)	O(2)—H(O2)	1·22 (O4)
C(10)–C(11)	1·489 (4)	O(10)–H(O2)	1·35 (O4)
C(10)–O(10)	1·266 (4)		

Table 10. *Bond angles* (°) *and their estimated standard deviations for clusianone*

C(3)—C(2)—O(2)	121·5 (2)	C(9)—C(5)—C(19)	110·2 (2)
C(3)—C(2)—C(1)	123·6 (2)	C(9)—C(5)—C(6)	105·6 (2)
O(2)—C(2)—C(1)	114·8 (2)	C(19)–C(5)—C(6)	113·0 (2)
C(2)—C(3)—C(4)	117·2 (2)	C(1)—C(9)—C(5)	114·4 (2)
C(2)—C(3)—C(10)	118·1 (2)	C(1)—C(9)—O(9)	122·4 (3)
C(4)—C(3)—C(10)	124·1 (2)	C(5)—C(9)—O(9)	122·9 (3)
C(3)—C(4)—O(4)	121·6 (2)	C(5)—C(19)–C(20)	114·0 (2)
C(3)—C(4)—C(5)	119·4 (2)	C(19)–C(20)–C(21)	126·3 (3)
O(4)—C(4)—C(5)	119·1 (3)	C(20)–C(21)–C(22)	124·7 (3)
C(2)—O(2)—H(O2)	110·2 (0)	C(20)–C(21)–C(23)	120·4 (3)
O(2)—H(O2)–O(10)	140·3 (0)	C(22)–C(21)–C(23)	114·9 (3)
C(3)—C(10)–O(10)	118·6 (2)	C(1)—C(29)–C(30)	113·5 (2)
C(3)—C(10)–C(11)	125·4 (3)	C(29)–C(30)–C(31)	128·0 (3)
O(10)–C(10)–C(11)	115·8 (3)	C(30)–C(31)–C(32)	125·3 (3)
H(O2)–O(10)–C(10)	111·2 (0)	C(30)–C(31)–C(33)	120·4 (3)
C(10)–C(11)–C(12)	122·3 (3)	C(32)–C(31)–C(33)	114·3 (3)
C(10)–C(11)–C(16)	117·3 (3)	C(5)—C(6)—C(7)	108·5 (2)
C(12)–C(11)–C(16)	120·1 (3)	C(5)—C(6)—C(17)	110·9 (2)
C(11)–C(12)–C(13)	119·6 (3)	C(5)—C(6)—C(18)	109·2 (2)
C(12)–C(13)–C(14)	120·1 (4)	C(7)—C(6)—C(17)	109·3 (2)
C(13)–C(14)–C(15)	120·2 (4)	C(7)—C(6)—C(18)	110·8 (2)
C(14)–C(15)–C(16)	120·1 (4)	C(17)–C(6)—C(18)	108·3 (2)
C(11)–C(16)–C(15)	119·7 (3)	C(6)—C(7)—C(8)	113·0 (2)
C(2)—C(1)—C(9)	108·8 (2)	C(6)—C(7)—C(24)	112·7 (2)
C(2)—C(1)—C(29)	110·4 (2)	C(8)—C(7)—C(24)	109·0 (2)
C(2)—C(1)—C(8)	109·1 (2)	C(1)—C(8)—C(7)	114·8 (2)
C(9)—C(1)—C(29)	112·7 (2)	C(7)—C(24)–C(25)	112·9 (2)
C(9)—C(1)—C(8)	105·4 (2)	C(24)–C(25)–C(26)	127·3 (3)
C(29)–C(1)—C(8)	110·3 (2)	C(25)–C(26)–C(27)	125·2 (3)
C(4)—C(5)—C(9)	110·2 (2)	C(25)–C(26)–C(28)	120·5 (3)
C(4)—C(5)—C(19)	107·8 (2)	C(27)–C(26)–C(28)	114·4 (3)
C(4)—C(5)—C(6)	110·1 (2)		

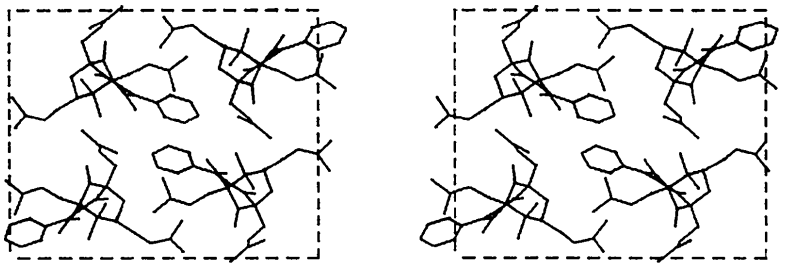

Fig. 3. Packing diagram of clusianone.

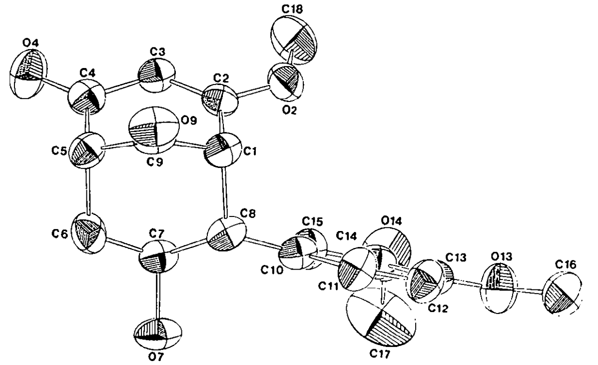

Fig. 4. Molecular structure of trimethylated catechinic acid.

Table 11. *Interatomic distances* (Å) *and their estimated standard deviations for trimethylated catechinic acid*

C(1)–C(2)	1·489 (8)	C(7)—C(8)	1·529 (7)
C(1)–C(8)	1·566 (7)	C(8)—C(10)	1·510 (7)
C(1)–C(9)	1·493 (8)	C(9)—O(9)	1·229 (6)
C(2)–O(2)	1·331 (6)	C(10)–C(11)	1·388 (7)
C(2)–C(3)	1·366 (7)	C(10)–C(15)	1·379 (8)
O(2)–C(18)	1·443 (9)	C(11)–C(12)	1·386 (9)
C(4)–C(3)	1·447 (8)	C(12)–C(13)	1·385 (8)
C(4)–O(4)	1·229 (6)	C(13)–O(13)	1·365 (7)
C(4)–C(5)	1·518 (8)	C(13)–C(14)	1·389 (8)
C(5)–C(6)	1·554 (8)	O(13)–C(16)	1·425 (9)
C(5)–C(9)	1·488 (7)	C(14)–O(14)	1·379 (7)
C(6)–C(7)	1·530 (8)	C(14)–C(15)	1·385 (8)
C(7)–O(7)	1·417 (6)	O(14)–C(17)	1·381 (8)

Another striking effect becomes evident upon examining the relative lengths of bonds in the fused ring systems. In general a bond in (I) is longer than the correspondingly similar bond in (II). This effect is attributed to the high degree of substitution of the rings in (I). In particular the bonds in the carbonyl bridge of (I) show appreciable lengthening due to the isopentenyl groups on C(1) and C(5) which eclipse the carbonyl group. The unusually long 1·603 (4) Å C(5)–C(6) bond is also associated with the high degree of substitution. Even though the bond has an almost perfectly staggered conformation, steric factors associated with the bond being between two highly substituted quaternary carbon atoms, one of which is located at a bridgehead position, are undoubtedly responsible for its lengthening. This type of bond has been observed to be unusually long in several other structures. Table 13 lists a number of precisely determined 'long' C–C bonds which have appeared in the recent literature.

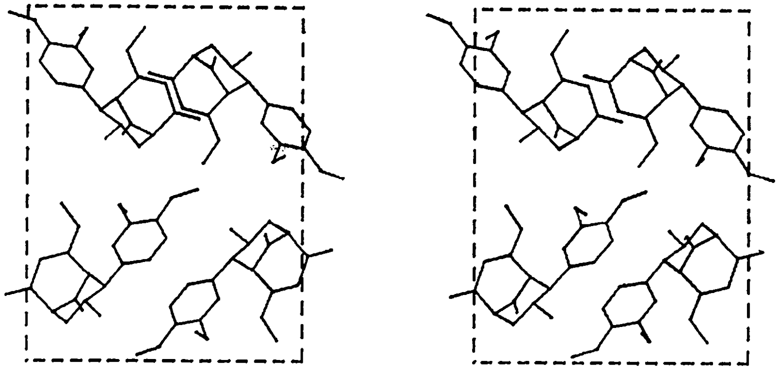

Fig. 5. Packing diagram of trimethylated catechinic acid.

Table 12. *Bond angles* (°) *and their estimated standard deviations for trimethylated catechinic acid*

C(2)–C(1)–C(8)	112·2 (4)	C(1)—C(8)—C(10)	111·9 (4)
C(2)–C(1)–C(9)	108·6 (4)	C(7)—C(8)—C(10)	115·4 (4)
C(8)–C(1)–O(9)	114·0 (4)	C(1)—C(9)—C(5)	113·2 (4)
C(1)–C(2)–O(2)	111·8 (4)	C(1)—C(9)—O(9)	124·0 (5)
C(1)–C(2)–C(3)	123·3 (5)	C(5)—C(9)—O(9)	122·8 (5)
O(2)–C(2)–C(3)	124·9 (5)	C(8)—C(10)–C(11)	119·0 (5)
C(2)–O(2)–C(18)	119·7 (5)	C(8)—C(10)–C(15)	122·9 (5)
C(2)–C(3)–C(4)	120·7 (5)	C(11)–C(10)–C(15)	117·9 (5)
C(3)–C(4)–O(4)	121·9 (5)	C(10)–C(11)–C(12)	121·8 (5)
C(3)–C(4)–C(5)	117·7 (5)	C(11)–C(12)–C(13)	119·6 (5)
O(4)–C(4)–C(5)	120·5 (5)	C(12)–C(13)–O(13)	124·4 (5)
C(4)–C(5)–C(6)	112·0 (4)	C(12)–C(13)–C(14)	119·1 (5)
C(4)–C(5)–C(9)	110·0 (5)	O(13)–C(13)–C(14)	116·5 (5)
C(6)–C(5)–C(9)	105·5 (4)	C(13)–O(13)–C(16)	119·7 (5)
C(5)–C(6)–C(7)	114·6 (5)	C(13)–C(14)–O(14)	119·3 (5)
C(6)–C(7)–O(7)	108·5 (5)	C(13)–C(14)–C(15)	120·4 (5)
C(6)–C(7)–C(8)	111·6 (4)	O(14)–C(14)–C(15)	120·1 (5)
O(7)–C(7)–C(8)	109·1 (4)	C(14)–O(14)–C(17)	116·7 (5)
C(1)–C(8)–C(7)	110·5 (4)	C(10)–C(15)–C(14)	121·2 (5)

With the exception of Bartell's (1966) 1·573 (4) Å electron diffraction result for hexamethylethane and Alden's (1968) 1·578 (2) Å bond in biadamantane, all of these bonds occur between quaternary carbon atoms which are members of rings or fused ring systems. Thus accurate X-ray evidence showing the importance of non-bonding interactions in determining C–C bond lengths is rapidly accumulating. It is interesting to note that if one assumes an average C–C bond to have a stretching energy proportional to 1000 cm^{-1}, the potential energy due to expanding the fused ring system of (I) relative to that of (II) is *ca* 10 kcal mol^{-1}.

Table 13. *Some precisely determined 'long' C–C bond distances*

Distance (Å)	Reference
1·570 (7)	Birnbaum (1973)
1·572 (3)	Ammon & Jensen (1967)
1·572 (7)	Shimanouchi & Sasada (1970)
1·573 (4)	O'Connell (1973)
1·573 (4)	Bartell (1966)
1·573 (6)	Milner-Srenger (1973)
1·574 (3)	Gilardi (1972)
1·574 (4)	Oh & Maslen (1968)
1·575 (3)	van Koningsveld (1973)
1·577 (2)	Ammon & Jensen (1967)
1·578 (2)	Alden, Kraut & Trayler (1968)
1·579 (4)	Ward, Templeton & Zalkin (1973)
1·583 (6)	Shirrell & Williams (1973)
1·583 (8)	Shimanouchi & Sasada (1970)
1·584 (2)	Alden, Kraut & Trayler (1968)
1·586 (7)	Birnbaum (1973)
1·593 (7)	Shimanouchi & Sasada (1970)
1·594 (7)	Shirrell & Williams (1973)
1·594 (6)	Shirrell & Williams (1973)
1·603 (4)	This work
1·628 (2)	Birnbaum (1972)
1·780 (7)	Bianchi, Morosi, Mugnoli & Simonetta (1973)
1·806 (7)	Bianchi, Morosi, Mugnoli & Simonetta (1973)

The remainder of the bond lengths are in good agreement with expected values except for C(4)–C(5) in (I) which is also long for an sp^3–sp^2 bond length and O(14)–C(17) in (II), which is strikingly short at 1·381 (8) Å. The methyl group represented by C(17) lies in a void in the structure and as a result has unusually large thermal parameters. Table 14 gives various corrections for the apparent bond shortening based on several models (Johnson, 1970) of thermal motion of C(17) and O(14). The 'riding' model gives a correction of 0·056 Å and a reasonable corrected bond length of 1·437 Å.

Table 14. *Correction to* O(14)–C(17) *bond distance for trimethylated catethinic acid* (*after Johnson*, 1970)

Model	Correction (Å)	Corrected bond length (Å)
Upper limit	$\{\alpha+\beta+2(\alpha\beta)^{1/2}\}/2d_o=0{\cdot}299$	1·680
Independent	$\{\alpha+\beta\}/2d_o=0{\cdot}155$	1·536
C(17) riding on O(14)	$\{\beta-\alpha\}/2d_o=0{\cdot}056$	1·437
Lower limit	$\{\alpha+\beta-2(\alpha\beta)^{1/2}\}/2d_o=0{\cdot}010$	1·391

$\alpha=0{\cdot}136$ $\beta=0{\cdot}292$ $2(\alpha\beta)^{1/2}=0{\cdot}399$ $d_o=1{\cdot}381$

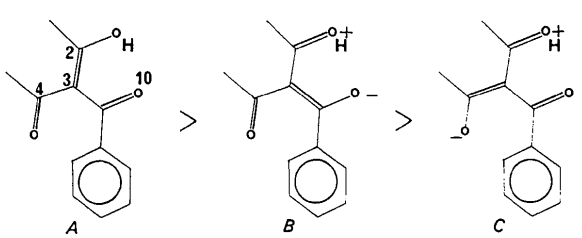

Fig. 6. Resonance in clusianone.

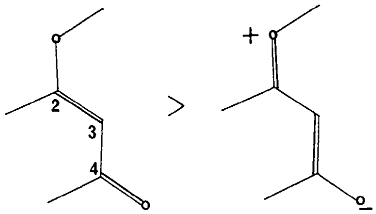

Fig. 7. Resonance in trimethylated catechinic acid.

(II) contains one strong intermolecular hydrogen bond which binds the individual molecules into chains along the **c** direction. The distance between O(7) in the first molecule and O(9) in the molecule related to the first by a unit translation along **c** is 2·783 Å. The location of the hydrogen was not discernible in a *ΔF* Fourier synthesis. (I) crystallizes with no intermolecular hydrogen bonds.

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The Crystal and Molecular Structure of the Enol Form of 3,3′-Dithiobis-(2,4-pentanedione)

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The crystal structure of the enol form of 3,3′-dithiobis-(2,4-pentanedione), $C_{10}H_{14}O_4S_2$, has been determined using three-dimensional X-ray diffraction data (Mo $K\alpha$ radiation) collected by counter methods. A report [Power & Jones, *Inorg. Nucl. Chem. Lett.* (1971), **7**, 887–890] outlining what is now known to be the incorrect structure, has previously been published. The compound crystallizes in the orthorhombic space group $Pna2_1$ and has cell dimensions $a=14{\cdot}852$ (5), $b=12{\cdot}264$ (4) and $c=6{\cdot}935$ (2) Å; $d_m=1{\cdot}36$, $d_c=1{\cdot}38$ g cm^{-3} for $Z=4$. The structure was refined, on F, by full-matrix, least-squares methods to an R value of 0·053 and wR of 0·038 for 1297 measured reflexions. The molecule exists as the enol tautomer and the short, intramolecular hydrogen bonds formed [O···O contacts of 2·418 (6) and 2·444 (7) Å] are asymmetric. There is evidence for alternating single and double bonds in the enol ring. The S–S distance is 2·082 (2) Å and the C–S distances are 1·744 (5) and 1·743 (4) Å. From comparison with other organic sulphides, a dependence of the C–S bond length on the state of hybridization of the carbon atom is indicated. The C–S–S–C torsion angle is 68·6°.

Introduction

Bis-β-diketones are very useful as ligands because of their ability to form polymeric chelate compounds with transition metals (Fernelius, 1956; Kluiber & Lewis, 1960; Oh, 1961; Oh & Bailar, 1962; Jones & Power, 1971). The enol tautomer is of particular interest because of the large downfield shift of the enol proton in the PMR spectrum (Dewar, Fergusson, Hentschel, Wilkins & Williams, 1964; Jones, 1969). Such shifts are indicative of very strong, intramolecular hydrogen bonding. Some of these compounds have already been studied by diffraction methods. In 3,3′-trithiobis-(2,4-pentanedione) (Power & Jones, 1971*a*), the O···O contact was very short and this has been confirmed by neutron diffraction studies (Power, Turner, Moore & Jones, 1975). Similar short contacts were found in 2,2′-dithiobis-(1-phenyl-1,3-butanedione) (Power & Jones, 1971*c*) and tetraacetylethane (Schaefer & Wheatley, 1966; Power, Turner & Moore, 1975).

A report on the X-ray structure of the present compound has been published (Power & Jones, 1971*b*, denoted P&J). Even though the structure had been refined to an R value $(R=\sum||F_o|-k|F_c||/\sum|F_o|)$ of 0·093, bond lengths differed significantly from expected values. Although this anomaly could be due to disorder, a possibility if the space group was $Pnam$ rather than the assumed $Pna2_1$, the electron-density difference map did not indicate it. The correct structure is now reported and the reason for the previously incorrect structure determination discussed.

Experimental

3,3′-Dithiobis-(2,4-pentanedione), ($acac_2S_2$), was prepared by the method of Vaillant (1894). Pale yellow crystals were recrystallized from acetone and then by slow sublimation. Two forms of the compound were identified, a fact overlooked in the previous study (P&J). One form, that reported here and the assumed