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The Crystal and Molecular Structure of a Mineral Diterpene, Bombiccite, $C_{20}H_{34}$

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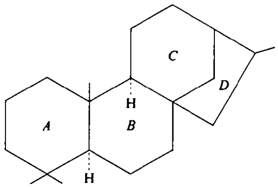
A natural product found in lignite mines has been assigned the structure of α-dihydrophyllocladene by crystal structure analysis. The crystals are triclinic, $P1$, $a = 11{\cdot}39$ (7), $b = 21{\cdot}29$ (5), $c = 7{\cdot}45$ (1) Å, $\alpha = 94{\cdot}6$ (1), $\beta = 101{\cdot}8$ (2), $\gamma = 81{\cdot}5$ (1)° and $Z = 4$. The structure has been solved by direct methods followed iteratively by Fourier syntheses and least-squares refinement of site occupation factors of the resulting peaks. The four independent molecules have the same configuration at the six chiral centres. Rings A, B and C assume the chair conformation with *trans* junctions, and ring D is an envelope.

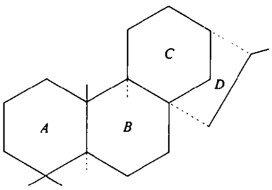
Introduction

Several organic minerals are in the Mineralogy Museum, University of Bologna, and one of them, simonellite, $C_{19}H_{24}$, has already been studied (Foresti & Riva di Sanseverino, 1969).

Bombiccite, present as a whitish crust on lignite from Castelnuovo di Valdarno, near Florence (Bombicci, 1869), was named after a former Professor of Mineralogy in Bologna, who encouraged the first chemical studies on the mineral. There was little evidence and much uncertainty about its chemistry (Ciusa & Galizzi, 1921), until a more recent crystallographic study by powder diffractometry (Pellizzer, 1955*a*) and then by single-crystal data (Pellizzer, 1955*b*) identified bombiccite with hartite (Strunz, 1974), chemically α-dihydrophyllocladene (I). The only structure from this family of natural diterpenes included on the Cambridge Crystallographic Data Files is phyllocladan-15-yl bromoacetate (Brown & Hall, 1976). Four other papers on the parent compound kauran (II) (Nakanishi, Goto, Ito, Natori & Nozoe, 1975) are available (Karle, 1972; Hanson, McLaughlin & Sim, 1972; Ferguson & Marsh, 1975; Taylor & Watson, 1976). The diterpenes display extraordinary variations of molecular skeleton and occurrence in nature. Bombiccite particularly has resisted microbiological degradation.



(I)



(II)

In view both of the uncertainty of its constitution and of the stereochemical problems, an X-ray crystallographic study of bombiccite was started as early as 1969.

Experimental

Samples of the mineral were collected, dissolved and purified by repeated crystallization from benzene. Plate-like colourless crystals were obtained by slow evaporation.

Preliminary crystal data and a full set of intensities were collected by rotation and Weissenberg photographs, using three crystals for the triclinic cell of

Table 1. *Crystal data for bombiccite*

$C_{20}H_{34}$	$M_r = 274$
m.p. 75 °C (α-dihydrophyllocladene 74 °C)	
$a = 11{\cdot}39$ (7) Å	$\alpha = 94{\cdot}6$ (1)°
$b = 21{\cdot}29$ (5)	$\beta = 101{\cdot}8$ (2)
$c = 7{\cdot}45$ (1)	$\gamma = 81{\cdot}5$ (1)
$V = 1707{\cdot}7$ Å^3	$Z = 4$
$d_c = 1{\cdot}07$ g cm^{-3}	$d_m = 1{\cdot}08$ g cm^{-3} (flotation)
Space group $P1$ (from structure solution)	$F(000) = 616$

bombiccite (Pellizzer, 1955*b*). Both density measurements and statistics from normalized structure factors confirmed all the data reported by Pellizzer, with $Z = 4$ and space group $P\bar{1}$. 3309 unique reflections were obtained after Lp corrections and merging from microdensitometer data.

At the beginning of 1975 a Philips PW diffractometer became available to us. The new crystal data (Table 1) obtained by the automatic cell-determination procedure, confirmed the previous observations. A crystal of dimensions 0·15 × 0·20 × 0·50 mm was mounted along **c**. Intensity data for all reflections with $2\theta < 50°$ were recorded using the $\omega/2\theta$ scan technique and Mo $K\alpha$ radiation ($\lambda = 0{\cdot}7107$ Å), scan period of 0·06° s^{-1} and scan width of 1·20°. 6109 unique reflections were measured of which 4415 had $I > 2{\cdot}5\sigma(I)$ based on counting statistics. A 5 s background count was taken on either side of the scan range. Intensities of three standard reflections were checked throughout the data collection. Lp corrections were applied, but none for absorption. Complex neutral-atom scattering factors were employed in all calculations (*International Tables for X-ray Crystallography*, 1974).

Structure solution and refinement

Repeated trials with all sorts of modifications of direct-methods versions failed to indicate a solution for several years. Speculation about a space-group error was encouraged by the presence of peculiar pairs of high E values belonging to planes differing by two in either h or k indices, but photographic reinvestigation, including precession methods, gave no hint of monoclinic symmetry.

Table 2. *Atom coordinates* ($\times 10^4$) *and isotropic temperature factors* (Å^2 × 10^3)

	x	*y*	*z*	*U*		*x*	*y*	*z*	*U*
C(011)	4901 (8)	532 (4)	2159 (13)	66 (2)	C(013)	9893 (7)	6158 (4)	4415 (11)	54 (2)
C(021)	4939 (10)	177 (5)	3913 (15)	87 (3)	C(023)	9859 (9)	5803 (4)	2538 (13)	72 (2)
C(031)	4139 (11)	563 (5)	5239 (16)	85 (3)	C(033)	10713 (10)	5982 (5)	1425 (16)	85 (3)
C(041)	4486 (9)	1234 (4)	5771 (13)	69 (2)	C(043)	10409 (9)	6735 (4)	1094 (13)	71 (2)
C(051)	4370 (7)	1652 (4)	4065 (11)	52 (2)	C(053)	10454 (7)	7152 (4)	2886 (10)	50 (2)
C(061)	5025 (7)	2244 (4)	4711 (10)	48 (2)	C(063)	9855 (7)	7852 (4)	2395 (11)	54 (2)
C(071)	4425 (8)	2708 (4)	6133 (12)	65 (2)	C(073)	10486 (9)	8180 (5)	1120 (13)	71 (2)
C(081)	5063 (10)	3294 (5)	6700 (15)	82 (3)	C(083)	9913 (12)	8872 (6)	734 (17)	95 (3)
C(091)	5333 (9)	3612 (5)	5052 (14)	78 (3)	C(093)	9576 (10)	9269 (5)	2480 (14)	83 (3)
C(101)	6115 (9)	3111 (5)	4048 (13)	71 (2)	C(103)	8773 (9)	8935 (5)	3258 (14)	77 (2)
C(111)	5246 (7)	2667 (4)	3143 (10)	51 (2)	C(113)	9620 (7)	8330 (4)	4068 (10)	50 (2)
C(121)	5784 (8)	2209 (4)	1677 (12)	61 (2)	C(123)	9029 (8)	8003 (4)	5382 (12)	66 (2)
C(131)	5113 (8)	1646 (4)	1051 (11)	59 (2)	C(133)	9649 (8)	7330 (4)	5883 (12)	62 (2)
C(141)	5118 (7)	1246 (4)	2682 (10)	51 (2)	C(143)	9667 (6)	6899 (3)	4137 (10)	45 (2)
C(151)	3659 (9)	483 (5)	870 (13)	74 (2)	C(153)	11081 (9)	5923 (5)	5756 (15)	79 (3)
C(161)	5912 (10)	159 (5)	1237 (16)	88 (3)	C(163)	8815 (10)	5977 (5)	5236 (15)	83 (3)
C(171)	3044 (7)	1830 (4)	3229 (11)	56 (2)	C(173)	11786 (8)	7101 (4)	3807 (12)	65 (2)
C(181)	4249 (8)	3796 (5)	3548 (13)	68 (2)	C(183)	10613 (9)	9292 (5)	4026 (14)	77 (2)
C(191)	3058 (10)	4142 (6)	4170 (16)	89 (3)	C(193)	11852 (11)	9436 (6)	3614 (18)	99 (3)
C(201)	4111 (7)	3150 (4)	2412 (11)	55 (2)	C(203)	10724 (8)	8634 (4)	4995 (12)	60 (2)
C(012)	−842 (9)	1123 (5)	7980 (13)	72 (2)	C(014)	5253 (8)	8149 (4)	7434 (12)	66 (2)
C(022)	−1089 (9)	918 (5)	5951 (14)	79 (3)	C(024)	4210 (9)	8581 (5)	8253 (14)	75 (2)
C(032)	−230 (9)	1134 (5)	4885 (13)	75 (2)	C(034)	4130 (9)	8402 (5)	10151 (14)	75 (2)
C(042)	−275 (8)	1874 (4)	5072 (12)	66 (2)	C(044)	3969 (8)	7689 (4)	10188 (12)	64 (2)
C(052)	−35 (7)	2144 (4)	7030 (11)	53 (2)	C(054)	4995 (7)	7211 (4)	9523 (10)	51 (2)
C(062)	−442 (8)	2882 (4)	7044 (11)	57 (2)	C(064)	4607 (7)	6531 (4)	9197 (11)	53 (2)
C(072)	259 (9)	3254 (4)	5935 (13)	71 (2)	C(074)	4418 (9)	6243 (5)	10958 (13)	71 (2)
C(082)	−188 (10)	3980 (5)	5965 (15)	85 (3)	C(084)	4068 (10)	5566 (5)	10668 (15)	79 (3)
C(092)	−335 (9)	4261 (5)	7876 (15)	81 (3)	C(094)	4787 (9)	5122 (5)	9390 (13)	74 (2)
C(102)	−1192 (10)	3926 (5)	8566 (16)	86 (3)	C(104)	4659 (9)	5446 (5)	7581 (14)	77 (3)
C(112)	−488 (8)	3247 (4)	8942 (12)	64 (2)	C(114)	5381 (7)	6015 (4)	8133 (11)	51 (2)
C(122)	−1099 (9)	2859 (5)	10132 (14)	73 (2)	C(124)	5643 (8)	6301 (4)	6404 (13)	69 (2)
C(132)	−667 (9)	2142 (5)	10118 (13)	74 (2)	C(134)	6061 (8)	6951 (4)	6775 (12)	61 (2)
C(142)	−834 (7)	1850 (4)	8168 (11)	58 (2)	C(144)	5127 (7)	7436 (4)	7586 (11)	54 (2)
C(152)	297 (10)	709 (5)	8990 (15)	85 (3)	C(154)	6475 (10)	8332 (6)	8371 (16)	89 (3)
C(162)	−1916 (11)	949 (6)	8800 (18)	101 (3)	C(164)	5033 (11)	8310 (6)	5357 (16)	95 (3)
C(172)	1338 (7)	1955 (4)	7810 (11)	55 (2)	C(174)	6166 (8)	7215 (4)	10919 (12)	64 (2)
C(182)	795 (9)	4106 (5)	9350 (14)	76 (2)	C(184)	6151 (8)	5036 (5)	10022 (12)	67 (2)
C(192)	1982 (9)	4220 (5)	8885 (14)	79 (3)	C(194)	6615 (10)	4894 (6)	11989 (16)	90 (3)
C(202)	730 (7)	3427 (4)	9908 (12)	59 (2)	C(204)	6503 (8)	5665 (4)	9376 (11)	59 (2)

Table 3. *Bond lengths* (Å)

C(011)–C(021)	1·55 (2)	C(012)–C(022)	1·52 (1)
C(011)–C(141)	1·58 (1)	C(012)–C(142)	1·54 (1)
C(011)–C(151)	1·55 (1)	C(012)–C(152)	1·55 (1)
C(011)–C(161)	1·55 (2)	C(012)–C(162)	1·57 (2)
C(021)–C(031)	1·58 (2)	C(022)–C(032)	1·52 (2)
C(031)–C(041)	1·54 (1)	C(032)–C(042)	1·56 (1)
C(041)–C(051)	1·58 (1)	C(042)–C(052)	1·51 (1)
C(051)–C(061)	1·55 (1)	C(052)–C(062)	1·57 (1)
C(051)–C(141)	1·59 (1)	C(052)–C(142)	1·58 (1)
C(051)–C(171)	1·51 (1)	C(052)–C(172)	1·55 (1)
C(061)–C(071)	1·58 (1)	C(062)–C(072)	1·58 (1)
C(061)–C(111)	1·61 (1)	C(062)–C(112)	1·56 (1)
C(071)–C(081)	1·52 (1)	C(072)–C(082)	1·55 (1)
C(081)–C(091)	1·55 (1)	C(082)–C(092)	1·53 (1)
C(091)–C(101)	1·53 (1)	C(092)–C(102)	1·48 (2)
C(091)–C(181)	1·51 (1)	C(092)–C(182)	1·52 (1)
C(101)–C(111)	1·49 (1)	C(102)–C(112)	1·56 (1)
C(111)–C(121)	1·56 (1)	C(112)–C(122)	1·58 (1)
C(111)–C(201)	1·56 (1)	C(112)–C(202)	1·51 (1)
C(121)–C(131)	1·51 (1)	C(122)–C(132)	1·53 (1)
C(131)–C(141)	1·54 (1)	C(132)–C(142)	1·52 (1)
C(181)–C(191)	1·58 (2)	C(182)–C(192)	1·52 (2)
C(181)–C(201)	1·57 (1)	C(182)–C(202)	1·55 (1)
C(013)–C(023)	1·52 (1)	C(014)–C(024)	1·58 (1)
C(013)–C(143)	1·58 (1)	C(014)–C(144)	1·56 (1)
C(013)–C(153)	1·55 (1)	C(014)–C(154)	1·57 (1)
C(013)–C(163)	1·58 (2)	C(014)–C(164)	1·51 (2)
C(023)–C(033)	1·51 (2)	C(024)–C(034)	1·52 (2)
C(033)–C(043)	1·62 (1)	C(034)–C(044)	1·56 (1)
C(043)–C(053)	1·54 (1)	C(044)–C(054)	1·56 (1)
C(053)–C(063)	1·58 (1)	C(054)–C(064)	1·56 (1)
C(053)–C(143)	1·59 (1)	C(054)–C(144)	1·60 (1)
C(053)–C(173)	1·52 (1)	C(054)–C(174)	1·51 (1)
C(063)–C(073)	1·56 (1)	C(064)–C(074)	1·56 (1)
C(063)–C(113)	1·58 (1)	C(064)–C(114)	1·57 (1)
C(073)–C(083)	1·54 (1)	C(074)–C(084)	1·54 (1)
C(083)–C(093)	1·57 (2)	C(084)–C(094)	1·55 (1)
C(093)–C(103)	1·47 (2)	C(094)–C(104)	1·53 (1)
C(093)–C(183)	1·47 (1)	C(094)–C(184)	1·51 (2)
C(103)–C(113)	1·57 (1)	C(104)–C(114)	1·54 (1)
C(113)–C(123)	1·55 (1)	C(114)–C(124)	1·57 (1)
C(113)–C(203)	1·51 (1)	C(114)–C(204)	1·55 (1)
C(123)–C(133)	1·54 (1)	C(124)–C(134)	1·52 (1)
C(133)–C(143)	1·53 (1)	C(134)–C(144)	1·55 (1)
C(183)–C(193)	1·58 (1)	C(184)–C(194)	1·49 (1)
C(183)–C(203)	1·60 (1)	C(184)–C(204)	1·59 (1)

Using a phenanthrene skeleton, molecular packing calculations by means of potential minimum energy (Coiro, Giglio & Quagliata, 1972) also proved unsuccessful.

With the diffractometer data the statistics strongly confirmed the centrosymmetric space group. This time the independent Ewald hemisphere had been fully scanned and there was no intensity fall-off at high θ values.

Finally, the constant presence of high peaks joined to their centrosymmetric image in E maps calculated using the *SHELX* system of programs (Sheldrick, 1976) induced us to try the non-centrosymmetric space group $P1$. A tricyclic fragment (partially incorrect, as revealed by the structure solution) obtained by unscrambling a double image from a $P\bar{1}$ E map, was extended by refinement of atom site occupancy factors followed by a sharpened Sim-weighted (Sim, 1961) Fourier synthesis. The unique peaks from this map were then used as atoms for further site occupancy factor refinement, and the process was repeated for several cycles. This procedure slowly produced a Fourier map where 80 correct C atoms were included among the first 81 peaks. The agreement factor at this stage was 0·31. Blocked cascade least-squares isotropic refinement reduced this value to 0·14. In this method, which considerably reduces the computer-time requirements for large structures, the refinement is divided into a number of full-matrix blocks (about 12 atoms in each). Since calculated partial structure factors are saved, it is necessary only to recalculate structure factor contributions for those atoms which refined in the previous block. The blocks are constituted differently on each pass through the atom list. When H atoms, positioned geometrically and riding on their respective C atoms, were introduced [so that the C—H vectors were constant in magnitude and direction but the C atoms were free to move, and no H atom was attached to C(16) or C(19)], the isotropic refinement converged slowly to an R value of 0·116 for the 4415 observed reflections. No further refinement was performed because of the prohibitive computer time required for a problem of this size. The weighting scheme was $w = 1/[\sigma^2(F_o) + 0{\cdot}0032F_o^2]$, where $\sigma^2(F_o)$ was derived from

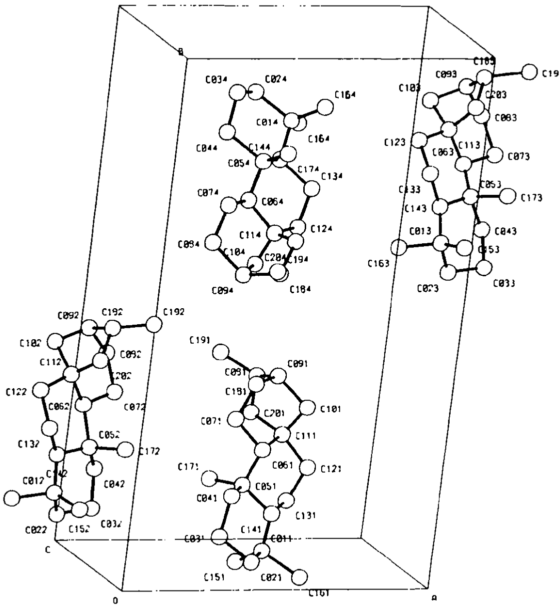


Fig. 1. A perspective view of the cell contents for bombiccite. The numbering is arbitrary.

Table 4. *Bond angles* (°)

C(021)–C(011)–C(141)	110·4 (7)	C(022)–C(012)–C(142)	108·6 (8)
C(021)–C(011)–C(151)	107·9 (8)	C(022)–C(012)–C(152)	109·9 (8)
C(021)–C(011)–C(161)	105·5 (8)	C(022)–C(012)–C(162)	106·8 (9)
C(141)–C(011)–C(151)	112·1 (7)	C(142)–C(012)–C(152)	116·7 (8)
C(141)–C(011)–C(161)	111·7 (8)	C(142)–C(012)–C(162)	109·7 (7)
C(151)–C(011)–C(161)	108·9 (9)	C(152)–C(012)–C(162)	104·7 (10)
C(011)–C(021)–C(031)	112·7 (8)	C(012)–C(022)–C(032)	113·7 (9)
C(021)–C(031)–C(041)	112·1 (10)	C(022)–C(032)–C(042)	110·9 (8)
C(031)–C(041)–C(051)	113·5 (8)	C(032)–C(042)–C(052)	114·2 (7)
C(041)–C(051)–C(061)	108·7 (6)	C(042)–C(052)–C(062)	108·9 (6)
C(041)–C(051)–C(141)	107·0 (7)	C(042)–C(052)–C(142)	109·1 (8)
C(041)–C(051)–C(171)	109·4 (7)	C(042)–C(052)–C(172)	106·9 (7)
C(061)–C(051)–C(141)	105·8 (7)	C(062)–C(052)–C(142)	107·4 (7)
C(061)–C(051)–C(171)	112·3 (7)	C(062)–C(052)–C(172)	113·6 (7)
C(141)–C(051)–C(171)	113·3 (6)	C(142)–C(052)–C(172)	110·7 (7)
C(051)–C(061)–C(071)	113·7 (7)	C(052)–C(062)–C(072)	114·2 (7)
C(051)–C(061)–C(111)	117·2 (6)	C(052)–C(062)–C(112)	117·9 (7)
C(071)–C(061)–C(111)	107·8 (6)	C(072)–C(062)–C(112)	108·5 (7)
C(061)–C(071)–C(081)	112·6 (9)	C(062)–C(072)–C(082)	112·9 (9)
C(071)–C(081)–C(091)	113·3 (8)	C(072)–C(082)–C(092)	113·2 (9)
C(081)–C(091)–C(101)	107·5 (8)	C(082)–C(092)–C(102)	109·6 (9)
C(081)–C(091)–C(181)	115·6 (9)	C(082)–C(092)–C(182)	113·2 (9)
C(101)–C(091)–C(181)	102·2 (8)	C(102)–C(092)–C(182)	100·0 (9)
C(091)–C(101)–C(111)	103·1 (9)	C(092)–C(102)–C(112)	104·1 (9)
C(061)–C(111)–C(101)	107·5 (6)	C(062)–C(112)–C(102)	107·8 (7)
C(061)–C(111)–C(121)	108·2 (7)	C(062)–C(112)–C(122)	109·5 (7)
C(061)–C(111)–C(201)	112·4 (7)	C(062)–C(112)–C(202)	112·8 (8)
C(101)–C(111)–C(121)	111·0 (8)	C(102)–C(112)–C(122)	112·7 (8)
C(101)–C(111)–C(201)	100·5 (8)	C(102)–C(112)–C(202)	99·4 (8)
C(121)–C(111)–C(201)	116·6 (6)	C(122)–C(112)–C(202)	114·2 (7)
C(111)–C(121)–C(131)	113·9 (8)	C(112)–C(122)–C(132)	115·0 (8)
C(121)–C(131)–C(141)	110·7 (7)	C(122)–C(132)–C(142)	111·8 (8)
C(011)–C(141)–C(051)	118·7 (8)	C(012)–C(142)–C(052)	117·8 (7)
C(011)–C(141)–C(131)	115·2 (7)	C(012)–C(142)–C(132)	115·7 (8)
C(051)–C(141)–C(131)	109·5 (7)	C(052)–C(142)–C(132)	110·3 (7)
C(091)–C(181)–C(191)	117·0 (9)	C(092)–C(182)–C(192)	116·0 (10)
C(091)–C(181)–C(201)	102·1 (7)	C(092)–C(182)–C(202)	105·0 (8)
C(191)–C(181)–C(201)	115·1 (8)	C(192)–C(182)–C(202)	116·6 (8)
C(111)–C(201)–C(181)	107·7 (6)	C(112)–C(202)–C(182)	107·2 (7)
C(023)–C(013)–C(143)	108·8 (7)	C(024)–C(014)–C(144)	108·8 (8)
C(023)–C(013)–C(153)	110·3 (7)	C(024)–C(014)–C(154)	105·6 (8)
C(023)–C(013)–C(163)	107·6 (8)	C(024)–C(014)–C(164)	110·1 (8)
C(143)–C(013)–C(153)	114·8 (7)	C(144)–C(014)–C(154)	110·1 (8)
C(143)–C(013)–C(163)	108·4 (7)	C(144)–C(014)–C(164)	114·0 (7)
C(153)–C(013)–C(163)	106·7 (9)	C(154)–C(014)–C(164)	107·9 (9)
C(013)–C(023)–C(033)	115·4 (9)	C(014)–C(024)–C(034)	113·1 (8)
C(023)–C(033)–C(043)	109·1 (9)	C(024)–C(034)–C(044)	112·2 (8)
C(033)–C(043)–C(053)	113·3 (9)	C(034)–C(044)–C(054)	114·1 (8)
C(043)–C(053)–C(063)	108·6 (6)	C(044)–C(054)–C(064)	109·8 (8)
C(043)–C(053)–C(143)	109·7 (7)	C(044)–C(054)–C(144)	106·8 (6)
C(043)–C(053)–C(173)	105·8 (7)	C(044)–C(054)–C(174)	109·9 (7)
C(063)–C(053)–C(143)	107·1 (7)	C(064)–C(054)–C(144)	107·6 (6)
C(063)–C(053)–C(173)	113·9 (7)	C(064)–C(054)–C(174)	111·3 (6)
C(143)–C(053)–C(173)	111·7 (7)	C(144)–C(054)–C(174)	111·3 (7)
C(053)–C(063)–C(073)	114·9 (7)	C(054)–C(064)–C(074)	114·3 (7)
C(053)–C(063)–C(113)	116·4 (6)	C(054)–C(064)–C(114)	117·5 (8)
C(073)–C(063)–C(113)	109·2 (7)	C(074)–C(064)–C(114)	109·0 (7)
C(063)–C(073)–C(083)	113·6 (9)	C(064)–C(074)–C(084)	114·9 (8)
C(073)–C(083)–C(093)	113·7 (10)	C(074)–C(084)–C(094)	113·5 (10)
C(083)–C(093)–C(103)	109·0 (9)	C(084)–C(094)–C(104)	108·7 (8)
C(083)–C(093)–C(183)	113·4 (10)	C(084)–C(094)–C(184)	115·2 (8)
C(103)–C(093)–C(183)	101·7 (9)	C(104)–C(094)–C(184)	100·6 (8)
C(093)–C(103)–C(113)	103·8 (9)	C(094)–C(104)–C(114)	103·9 (8)
C(063)–C(113)–C(103)	107·6 (6)	C(064)–C(114)–C(104)	107·6 (8)
C(063)–C(113)–C(123)	109·7 (7)	C(064)–C(114)–C(124)	110·2 (7)
C(063)–C(113)–C(203)	113·1 (7)	C(064)–C(114)–C(204)	113·2 (7)
C(103)–C(113)–C(123)	111·5 (8)	C(104)–C(114)–C(124)	111·3 (8)

Table 4 (*cont.*)

C(103)–C(113)–C(203)	99·6 (8)	C(104)–C(114)–C(204)	99·4 (7)
C(123)–C(113)–C(203)	114·8 (7)	C(124)–C(114)–C(204)	115·5 (8)
C(113)–C(123)–C(133)	114·8 (8)	C(114)–C(124)–C(134)	114·2 (7)
C(123)–C(133)–C(143)	110·0 (7)	C(124)–C(134)–C(144)	111·3 (8)
C(013)–C(143)–C(053)	116·4 (6)	C(014)–C(144)–C(054)	118·3 (7)
C(013)–C(143)–C(133)	115·9 (6)	C(014)–C(144)–C(134)	115·0 (8)
C(053)–C(143)–C(133)	110·3 (6)	C(054)–C(144)–C(134)	109·5 (6)
C(093)–C(183)–C(193)	118·3 (10)	C(094)–C(184)–C(194)	116·2 (9)
C(093)–C(183)–C(203)	104·8 (9)	C(094)–C(184)–C(204)	102·7 (8)
C(193)–C(183)–C(203)	113·6 (8)	C(194)–C(184)–C(204)	116·4 (9)
C(113)–C(203)–C(183)	105·8 (7)	C(114)–C(204)–C(184)	109·3 (8)

Table 5. *Average bond lengths* (Å)

a, mean value; *b*, mean value standard deviation, $\frac{1}{4}[\sum_{i=1}^{4}\sigma_i^2]^{1/2}$; *c*, maximum spread from mean value.

	a	*b*	*c*
C(01)–C(02)	1·542	0·006	0·038
C(01)–C(14)	1·565	0·005	0·015
C(01)–C(15)	1·555	0·005	0·015
C(01)–C(16)	1·552	0·010	0·042
C(02)–C(03)	1·532	0·010	0·048
C(03)–C(04)	1·570	0·005	0·050
C(04)–C(05)	1·547	0·005	0·037
C(05)–C(06)	1·565	0·005	0·015
C(05)–C(14)	1·590	0·005	0·010
C(05)–C(17)	1·522	0·005	0·028
C(06)–C(07)	1·570	0·005	0·010
C(06)–C(11)	1·580	0·005	0·030
C(07)–C(08)	1·537	0·005	0·017
C(08)–C(09)	1·550	0·006	0·020
C(09)–C(10)	1·502	0·008	0·032
C(09)–C(18)	1·502	0·006	0·032
C(10)–C(11)	1·540	0·005	0·050
C(11)–C(12)	1·565	0·005	0·015
C(12)–C(20)	1·532	0·005	0·028
C(12)–C(13)	1·525	0·005	0·015
C(13)–C(14)	1·535	0·005	0·015
C(18)–C(19)	1·545	0·010	0·055
C(18)–C(20)	1·577	0·005	0·027

counting statistics. This resulted in a flat variance in terms of sin θ and the magnitude of $|F_o|$.*

C atom coordinates and thermal parameters are listed in Table 2. The numbering is arbitrary and each molecule is distinguished by the last digit. H coordinates are not reported because they were positioned geometrically and constrained during the refinement.

Tables 3, 4, 5 and 6 list bond distances and angles. Programs written by GMS were employed for the structure solution and refinement; the drawings were made by using *PLUTO* (Motherwell, 1976). The literature searches were performed with the Cambridge Crystallographic Data Centre System of programs.

Table 6. *Average bond angles* (°)

a, mean value; *b*, mean value standard deviation, $\frac{1}{4}[\sum_{i=1}^{4}\sigma_i^2]^{1/2}$; *c*, maximum spread from mean value.

	a	*b*	*c*
C(02)–C(01)–C(14)	109·1	0·37	1·3
C(02)–C(01)–C(15)	108·4	0·39	2·8
C(02)–C(01)–C(16)	108·5	0·41	3·0
C(14)–C(01)–C(15)	113·4	0·37	3·3
C(14)–C(01)–C(16)	110·9	0·36	3·1
C(15)–C(01)–C(16)	107·0	0·46	2·3
C(01)–C(02)–C(03)	113·7	0·42	1·7
C(02)–C(03)–C(04)	111·1	0.44	2.0
C(03)–C(04)–C(05)	113·8	0.40	0.5
C(04)–C(05)–C(06)	109·0	0·33	0·8
C(04)–C(05)–C(14)	108·1	0·35	1·6
C(04)–C(05)–C(17)	108·0	0·35	2·2
C(06)–C(05)–C(14)	107·0	0·34	1·2
C(06)–C(05)–C(17)	112·8	0·34	1·5
C(14)–C(05)–C(17)	111·7	0·34	1·6
C(05)–C(06)–C(07)	114·3	0·35	0·6
C(05)–C(06)–C(11)	117·2	0·34	0·7
C(07)–C(06)–C(11)	108·6	0·34	0·8
C(06)–C(07)–C(08)	113·5	0·44	1·4
C(07)–C(08)–C(09)	113·4	0·46	0·3
C(08)–C(09)–C(10)	108·7	0·42	1·2
C(08)–C(09)–C(18)	114·3	0·45	1·3
C(10)–C(09)–C(18)	101·1	0·42	1·1
C(09)–C(10)–C(11)	103·7	0·43	0·4
C(06)–C(11)–C(10)	107·6	0·34	0·1
C(06)–C(11)–C(12)	109·4	0·35	1·2
C(06)–C(11)–C(20)	112·9	0·36	0·5
C(10)–C(11)–C(12)	111·5	0·40	1·2
C(10)–C(11)–C(20)	99·8	0·39	0·7
C(12)–C(11)–C(20)	115·3	0·35	1·3
C(11)–C(12)–C(13)	114·5	0·39	0·6
C(12)–C(13)–C(14)	110·8	0·37	1·0
C(01)–C(14)–C(05)	117·8	0·35	1·4
C(01)–C(14)–C(13)	115·4	0·36	0·5
C(09)–C(18)–C(19)	116·8	0·48	1·5
C(09)–C(18)–C(20)	103·6	0·40	1·4
C(19)–C(18)–C(20)	115·5	0·42	1·9
C(11)–C(20)–C(18)	107·4	0·35	1·9

Discussion

Fig. 1 shows a perspective view of the unit-cell contents, and indicates the arbitrary numbering scheme used in all the tables.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 33217 (27 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The molecules have the same configuration at the six asymmetric centres. The four identical molecules occupy a crystallographic asymmetric unit, in this case the unit cell.

An approximate inversion centre appears to relate molecules 1 and 4, whereas molecules 2 and 3 are related by an approximate $\frac{1}{2}b$ translation. This geometrical distribution in the cell may account for the indication of a symmetry centre by the statistical distributions and the recurring pairs of high E values with constant differences of two in h and k indices.

This structure offers the rare opportunity of comparing four chemically equal but crystallographically independent molecules. The average bond distances (and deviations) for the 23 sp^3–sp^3 bonds are 1·55 (1), 1·54 (1), 1·55 (1) and 1·55 (1) Å for the four molecules respectively.

The deviations of bond angles from idealized values appear to be consistent with the strain induced by the fused five-membered ring and the 1,3-diaxial repulsion between C(15) and C(17). Ring *D* has an envelope conformation as usually found in phyllocladan and kauran derivatives. The low value of the deformed tetrahedral angle C(10)–C(11)–C(20) is a consistent feature of these molecules.

Rings *A*, *B* and *C* are in the chair conformation: the angle C(1)–C(14)–C(5) is considerably greater than tetrahedral, which is probably a consequence of the short intermolecular contacts between the axial methyls (Brown & Hall, 1976). The mean contact distance is 3·26 Å, compared with 3·24 Å found by Brown & Hall. There are no intermolecular C···C contacts less than 3·7 Å.

The experimental conformations of the four molecules are quantitatively described in Fig. 2, which lists average torsion angles internal to the rings. The consistent molecular shape indicates that the frequently invoked packing forces have little effect on the molecular conformation. To some extent the absence of any significant effect had been suggested by van der Waals potential-energy calculations on steroids (Foresti Serantoni, Krajewski, Mongiorgi, Riva di Sanseverino & Sabatino, 1975) and on anti-epileptic drugs (Mongiorgi, Riva di Sanseverino & Sabatino, 1976).

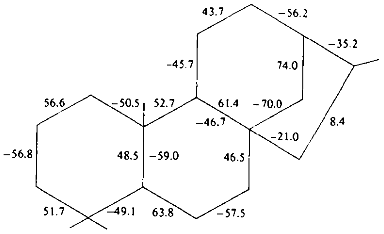

Fig. 2. Average torsion angles (°) for bombiccite. Average deviation is 1·4° and maximum deviation 3·7°. The torsion angle *w*(*ABCD*) is defined as the angle between vector *BA* and vector *CD* when viewed down *BC*; *w* is positive if *BA* has to be rotated clockwise into *CD*.

Professor P. Gallitelli, former Director of the Mineralogy Institute, University of Bologna, kindly selected mineral samples of bombiccite. The diffractometer at the Centro di Cristallografia Strutturale del CNR, Pavia, was used for the data collection. One of us (LRS) is grateful to the Royal Society of London for a grant in Cambridge within the European Scientific Exchange Program. This work was financed by the Consiglio Nazionale delle Ricerche, Rome.

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