Discussion. Coordinates and U_{eq} values are listed in Table 1 for the non-H atoms. Bond lengths and angles are shown in Table 2.* The molecular structure is illustrated in Fig. 1, which also shows the atomic-numbering scheme adopted. The etheno bridge is in the 6β,14β position and the acetyl substituent is in the 8β position of the morphinan skeleton, which means that the Diels–Alder reaction of 6-demethoxy-β-dihydrothebaine (1) with methyl vinyl ketone occurs from the α face of the diene system as was observed earlier for the 7β-substituted adduct (van Koningsveld, Lie & Maat, 1984). This is in contrast to the Diels–Alder reaction of thebaine itself or thebaine analogues with the 4,5α-epoxy ring closed, where the addition takes place from the β face (van Koningsveld, Maat & Lie, 1984), which may be explained by release of the strain in the thebaine molecule after opening of the epoxy ring. In the case of 6-methoxymorphinan-6,8-dienes the electronic effect of the 6-methoxy group contributes to the formation of the 7-substituted ethenomorphinans as the major product. Obviously, the absence of the 6-methoxy group allows cycloaddition of methyl vinyl ketone in two ways, yielding a mixture of the 7β- and the 8β-acetyl substituted isomers. The substituents are in the β position, both directed towards the double bond of the etheno bridge, in agreement with the Diels '*endo* rule'. Conversion of these new compounds into etorphine-like derivatives may extend the knowledge of structure–activity relationships of opiates.

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* Lists of structure factors, anisotropic temperature factors of the non-H atoms and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44040 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Structure and Thermal Motion of Triphenylboroxin

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Abstract. $C_{18}H_{15}B_3O_3$, $M_r = 311·7$, monoclinic, $P2_1/c$, $a = 10·715$ (2), $b = 13·652$ (3), $c = 11·703$ (2) Å, $\beta = 100·38$ (1)°, $V = 1683·9$ (6) Å^3, $Z = 4$, $D_x = 1·230$ g cm^{-3}, λ(Mo $K\alpha$) (graphite monochromator) = 0·71073 Å, $\mu = 0·74$ cm^{-1}, $F(000) = 648$, $T = 295$ (1) K, $R = 0·041$ for 130 variables (group refinement incorporating the **TLS** model for rigid-body motion) and the 758 unique reflections having $I > 3\sigma(I)$. The weighted R factor based on F^2 for all 3851 unique reflections is 0·100. The central B_3O_3 ring is found to be nearly planar, but has a small envelope distortion; one of the B atoms is displaced by 0·119 (7) Å out of the plane of the other five atoms. The average B—O bond length is 1·386 (2) Å. The molecular dimensions determined are similar to those found previously for the related compounds 1,3,5-triphenylbenzene and *sym*-triphenyltriazine, but the conformations of the three molecules differ. The phenyl rings in the hydrocarbon adopt a propeller-like arrangement, while in the boroxin and triazine the phenyl groups are nearly coplanar with the central B_3O_3 or C_3N_3 ring. Possible relationships between thermal-motion descriptions and the intramolecular potential-energy surfaces for these molecules are considered.

Introduction. The structure of triphenylboroxin is of interest because of the possibility that the filled 2*p* orbitals on the O atoms might interact with the empty 2*p* orbitals on the B atoms to produce a conjugated system. A search of the May 1986 version of the Cambridge Structural Database (Allen, Kennard & Taylor, 1983) for the B_3O_3 ring fragment revealed only two full determinations (Yalpani & Boese, 1983) of structures other than polyborates. Both of them contain

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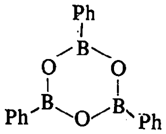
the triphenylboroxin molecule, but in each case one of the three B atoms is four-coordinate as a result of adduct formation with a nitrogen base. We were also interested in comparing the conformation of the title molecule with the conformations of the related molecules 1,3,5-triphenylbenzene (Lin & Williams, 1975) and *sym*-triphenyltriazine (Damiani, Giglio & Ripamonti, 1965; Lindeman, Shklover, Struchkov, Mitina & Pankratov, 1984).



Experimental. Triphenylboroxin (Alfa Products); colorless parallelepiped, 0·18 × 0·20 × 0·30 mm grown from petroleum ether and mounted in air; Enraf–Nonius CAD-4*F* diffractometer; 22 reflections having $8·9 \le \theta \le 13·8^\circ$ used to determine lattice parameters; ω–2θ scans; no absorption correction; $\theta \le 27·5^\circ$ [$(\sin\theta)/\lambda \le 0·650$ Å^{-1}]; quadrant of data with $0 \le h \le 15$, $0 \le k \le 17$, $-13 \le l \le 13$; average intensity loss for three control reflections of 11·4% overall (corrected); 3851 unique reflections measured; 758 data having $I > 3\sigma(I)$ used for refinement; structure solved using direct methods; computer programs as described previously (Brock & Webster, 1976; Brock, Blackburn & Haller, 1984); scattering factors from Cromer & Waber (1974).

Crystals of triphenylboroxin scatter very poorly at room temperature. Intensity loss with time, probably as a result of sublimation, is a problem. We collected full data sets at room temperature on two crystals, one of which was covered with silicone grease, and examined several others. Even in the best case fewer than 20% of the measured reflections had $I > 3\sigma(I)$. Several crystals examined at lower temperatures (*ca* 170 K and below) appeared to have undergone a phase transition. Peaks were substantially wider than at room temperature and some could not be indexed at all; the fit of the calculated to the observed setting angles for the reflections that could be assigned indices was poor.

Isotropic refinement for the O, C and B atoms, with H atoms included as fixed contributions at calculated positions, converged with R, $wR = 0·068$, 0·075 for 97 variables. The error in an observation of unit weight was 3·32, and peaks in a final difference Fourier synthesis had heights 0·28 to −0·22 e Å^{-3}. The bond lengths and angles were normal, and the patterns of the isotropic displacement parameters appeared reasonable (see Fig. 3).

With only 758 reflections having $I > 3\sigma(I)$, full anisotropic refinement, which would have required 217 variables, seemed to be out of the question. We did not consider it appropriate to include the weaker data in the refinement since their intensities had not been measured carefully [rate of prescan was 7° min^{-1} in ω; no final scan was made if $I/\sigma(I) < 1·4$ during prescan]. Crystal decomposition precluded more leisurely data collection, and an apparent phase transition (see above) ruled out a low-temperature study. Given the shortage of observations, we decided instead to treat the phenyl rings as rigid groups ($r_{\rm C-C} = 1·40$, $r_{\rm C-H} = 1·04$ Å) using a procedure (Brock *et al.*, 1984) that incorporates the **TLS** model (Cruickshank, 1956; Schomaker & Trueblood, 1968) for rigid-body motion. There was, however, one problem: the disposition of the C atoms of an idealized C_6H_5 ring, which lie on a circle, introduces a near singularity into the **TLS** description. We removed this singularity by taking the group origin at the center of the circle and then fixing the value of the component of the translation tensor in the direction normal to the ring. The **T**, **L** and **S** tensors are referred to an orthonormal axial system; we set x parallel to the vector RnC4–RnC1 (see Fig. 1) and z perpendicular to the phenyl plane. The T^{33} values were set equal to 0·0500 Å^2 based on our previous experience; final refined values for T^{11} and T^{22} have similar magnitudes [0·056 (2), 0·056 (2), 0·057 (2) Å^2 for the three T^{11} values; 0·074 (2), 0·078 (2), 0·078 (2) Å^2 for the three T^{22} values]. It must be noted that this choice affects the values determined for L^{11} and L^{22}, so that the physical significance of these quantities is open to question.

Final refinement on F magnitudes; R, $wR = 0·041$, 0·041 for 130 variables; wR (on F^2) = 0·100 for all 3851 data (negative intensities set to 0·0); error in an observation of unit weight = 1·84; $w = 4I/[\sigma^2(I)]$ where $[\sigma^2(I)]$ includes a term $(0·02I)^2$; maximum Δ/σ in last cycle of 0·19; features in final difference Fourier synthesis have heights 0·11 to −0·14 e Å^{-3}; of the 3093 reflections omitted from the refinement, none has $|I_o - I_c| > 3\sigma(I_o)$.

The molecular structure and the atom-numbering scheme are shown in Fig. 1, a side-on view of the molecule is given in Fig. 2, and the crystal packing is displayed in Fig. 3. Atomic coordinates are listed in Table 1, and some bond lengths, bond angles, and conformation angles are given in Table 2.*

Discussion. The relationships between the structures of the following five compounds are of interest: triphenylboroxin (hereafter, TPHBRX); the adducts of triphenylboroxin (Yalpani & Boese, 1983) with 1,4-

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* The refined atomic displacement parameters, the H-atom parameters, full thermal-motion descriptions for triphenylboroxin and 1,3,5-triphenylbenzene, and the observed and calculated structure-factor amplitudes [$I > 3\sigma(I)$] and intensities [$I \le 3\sigma(I)$] have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44000 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

diaminobenzene (CANIXY) and 1,4-diazabicyclo[2.2.2]octane (CANXOE); 1,3,5-triphenylbenzene (Lin & Williams, 1975; hereafter, TPHBEN); and *sym*-triphenyltriazine (Lindeman *et al.*, 1984; hereafter, TPTRAZ). The structure of the fourth member of this series, *B*-triphenylborazine, has not been reported.

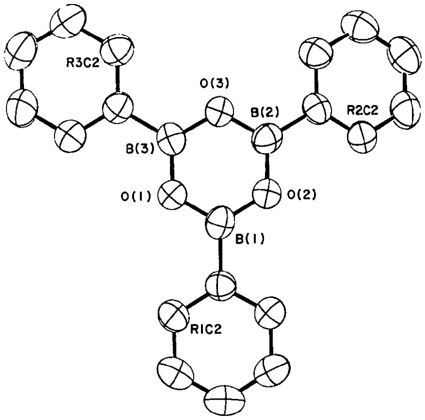


Fig. 1. Perspective drawing of the molecular structure of triphenylboroxin showing the atom-numbering scheme. The *RnCm* atoms are numbered sequentially around the rings, and *Rn*C1 is attached to B(*n*). In this and the following drawings the shapes of the ellipsoids correspond to 50% probability contours of atomic displacement, and the H atoms have been omitted for the sake of clarity.

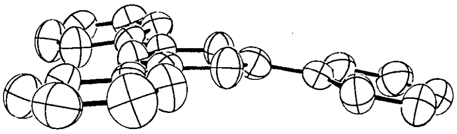


Fig. 2. Approximate edge-on view of the nearly planar structure of triphenylboroxin. Ring (2) is to the right of the B_3O_3 ring, and ring (1) is in front of ring (3).

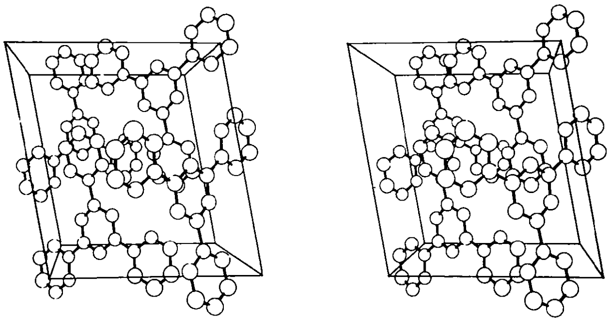


Fig. 3. Stereoscopic view of the unit cell of triphenylboroxin. The *a* axis points from left to right, the *c* axis upwards, and the *b* axis into the plane of the paper. This drawing was made using the isotropic displacement parameters from a converged refinement (see text).

The bond angles in the B_3O_3 ring (see Tables 2 and 3) are very near the 120° values expected if the bonds are formed from sp^2-hybrid orbitals. Even the variation in the values between the O—B—O and B—O—B angles echoes the pattern seen in TPHBEN for the C—C(Ph)—C and C—C(H)—C angles. The B_3O_3 ring in TPHBRX is almost planar, but it does display a small distortion of the envelope type (see Fig. 2). The root-mean-square (r.m.s.) deviation of the atoms O(1), B(1), O(2), O(3) and B(3) from their least-squares plane is only 0·008 (5) Å; the atom B(2) deviates from this plane by 0·119 (7) Å. The B_3O_3 rings in the two

Table 1. *Positional and displacement parameters for the atoms of triphenylboroxin*

	x	y	z	B_{eq}(Å^2)
O(1)	0·2453 (4)	0·5038 (3)	0·0280 (3)	5·0 (1)
O(2)	0·1767 (3)	0·5748 (3)	0·1916 (4)	5·3 (1)
O(3)	0·3496 (3)	0·4637 (3)	0·2193 (3)	5·0 (1)
B(1)	0·1645 (7)	0·5663 (5)	0·0727 (7)	4·8 (3)
B(2)	0·2620 (8)	0·5181 (5)	0·2669 (6)	4·9 (3)
B(3)	0·3405 (7)	0·4529 (5)	0·1003 (7)	4·9 (3)
*R*1C1	0·0609 (3)	0·6244 (2)	−0·0084 (3)	4·6
*R*1C2	0·0424 (3)	0·6120 (2)	−0·1291 (3)	5·4
*R*1C3	−0·0528 (3)	0·6648 (3)	−0·2011 (2)	6·1
*R*1C4	−0·1295 (3)	0·7300 (2)	−0·1524 (3)	6·3
*R*1C5	−0·1110 (3)	0·7424 (2)	−0·0318 (3)	6·8
*R*1C6	−0·0158 (3)	0·6896 (3)	0·0402 (2)	5·9
*R*2C1	0·2575 (3)	0·5133 (3)	0·3972 (2)	4·5
*R*2C2	0·1635 (3)	0·5642 (2)	0·4417 (3)	5·6
*R*2C3	0·1593 (3)	0·5593 (2)	0·5604 (3)	6·5
*R*2C4	0·2492 (4)	0·5036 (3)	0·6347 (2)	6·5
*R*2C5	0·3433 (3)	0·4527 (2)	0·5901 (3)	6·5
*R*2C6	0·3475 (3)	0·4575 (2)	0·4714 (3)	5·5
*R*3C1	0·4334 (3)	0·3859 (2)	0·0504 (3)	4·7
*R*3C2	0·5369 (3)	0·3434 (2)	0·1237 (2)	5·2
*R*3C3	0·6186 (3)	0·2806 (2)	0·0778 (3)	6·3
*R*3C4	0·5968 (3)	0·2602 (2)	−0·0414 (3)	6·7
*R*3C5	0·4933 (4)	0·3027 (3)	−0·1147 (2)	7·3
*R*3C6	0·4116 (3)	0·3656 (2)	−0·0688 (3)	6·4

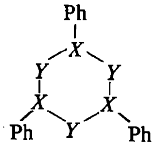
E.s.d.'s in the least-significant figure(s) are given in parentheses in this and the subsequent tables. The equivalent displacement parameter is defined as $\frac{4}{3}$tr($\boldsymbol{\beta}$.**G**), where $\beta_{ij} = 2\pi^2 a_i^* a_j^* U_{ij}$.

Table 2. *Selected distances* (Å), *angles* (°), *and conformation angles* (°) *for triphenylboroxin*

O(1)	B(1)			1·384 (9)	B(1)	O(2)		1·378 (10)
O(2)	B(2)			1·386 (8)	B(2)	O(3)		1·390 (9)
O(3)	B(3)			1·386 (9)	B(3)	O(1)		1·389 (8)
B(1)	*R*1C1			1·544 (8)	B(2)	*R*2C1		1·535 (8)
B(3)	*R*3C1			1·543 (9)				
B(3)	O(1)	B(1)		121·3 (5)	O(1)	B(1)	O(2)	118·8 (5)
B(1)	O(2)	B(2)		121·8 (5)	O(2)	B(2)	O(3)	117·3 (6)
B(2)	O(3)	B(3)		122·0 (5)	O(3)	B(3)	O(1)	118·0 (6)
O(1/2)	B(1)	*R*1C1	*R*1C2/6	3·1 (3)*				
O(2/3)	B(2)	*R*2C1	*R*2C2/6	2·9 (5)				
O(3/1)	B(3)	*R*3C1	*R*3C2/6	7·8 (5)				

* These values are averages of the four conformation angles calculated around the bonds B(*n*)—*Rn*C1. The standard deviations of these mean values are estimated from the variance of the individual values around the mean.

Table 3. *Comparisons of some average bond lengths* (Å), *bond angles* (°) *and conformation angles* (°) *for triphenylboroxin* (*TPHBRX*), *two adducts of triphenylboroxin* (*CANIXY, CANXOE*), 1,3,5-*triphenylbenzene* (*TPHBEN*), *and sym-triphenyltriazine* (*TPTRAZ*)



	TPHBRX	CANIXY/ CANXOE[a]	TPHBEN	TPTRAZ[b]
X, *Y*	B, O	B, O	C, C(H)	C, N
$\langle X\text{–}Y\rangle^c$	1·386 (2)	1·376 (7)	1·394 (2)	1·337 (1)
$\langle X\text{–C}\rangle$	1·540 (3)	1·565 (8)	1·488 (2)	1·482 (1)
$\langle X\text{–}Y\text{–}X\rangle$	121·7 (2)	120·8 (4)	121·4 (3)	115·3 (1)
$\langle Y\text{–}X\text{–}Y\rangle$	118·0 (4)	119·8 (2)	118·7 (2)	124·7 (1)
$\langle \text{C–C–}X\text{–}Y\rangle_i$	3 (1)	10 (2); 3 (2)	39 (1)	10 (1)
	3 (1)	18 (1); 2 (1)	36 (1)	6 (1)
	8 (1)		35 (1)	6 (1)

Notes: (*a*) No bond length or angle including a four-coordinate B atom has been included in this tabulation. In both compounds one of the three B atoms in the central B_3O_3 ring is four-coordinate. (*b*) Values calculated from the coordinates of Lindeman *et al.* (1984). (*c*) Averages are unweighted. Numbers in parentheses are standard deviations of the means as estimated from the width of the distributions.

adducts are also nearly planar; in both the r.m.s. deviation of the B and O atoms from the six-atom planes is 0·028 Å. The O—B—O angle at the four-coordinate B atom narrows to 113·3 (2)° in the adducts, and the neighboring B—O—B angles widen to 122·9 (1)° in compensation, but the other four bond angles in the ring are very near 120°. If structural criteria alone were considered, the B_3O_3 ring would probably be judged at least partially aromatic.

In all three of the triphenylboroxin structures the phenyl rings attached to three-coordinate B atoms are approximately coplanar with the B_3O_3 ring (see Fig. 2 and average conformation angles in Table 3). The four rings also approach coplanarity in the triazine structure. In contrast, the three phenyl rings in 1,3,5-triphenylbenzene are twisted by *ca* 37° relative to the central ring to give a propeller-like arrangement. Crystal-packing effects may play a role in determining the overall molecular conformations of these molecules, but it also seems likely that the lone pairs of electrons on the O and N atoms are less demanding sterically than are the H atoms that replace them in the hydrocarbon analogue.

Even if the steric requirements of the lone pairs of electrons on the O atoms are modest, it is probable that the conformation of triphenylboroxin in which the three C—C—B—O conformation angles are all zero corresponds to a small energy maximum. If 1,3,5-triphenylbenzene follows the model of several other simply substituted biphenyls (Almenningen, Bastiansen, Fernholt, Cyvin, Cyvin & Samdal, 1985), the conjugation energy gained from a coplanar arrangement of the central and peripheral rings is not sufficient to offset the resulting repulsions between the *ortho* H atoms. Similar arguments can be made for triphenylboroxin and *sym*-triphenyltriazine, except that in these molecules the magnitudes of both types of energy terms are likely to be smaller. We expect then that the nearly planar molecule seen in the TPHBRX structure is farther away from its lowest energy conformation than is the propeller-shaped molecule observed in the TPHBEN structure. If so, and if the conjecture is correct that torsional amplitudes observed in the crystalline phase can be correlated with position on the intramolecular potential-energy surface (Brock, Schweizer & Dunitz, 1985), then the amplitudes of the intramolecular torsions about the B—C bonds in TPHBRX should be larger than the corresponding amplitudes in TPHBEN. A similar prediction could be made for TPTRAZ, but reliable anisotropic displacement parameters do not seem to be available for that structure.

The average value of B_{eq} in TPHBRX for the 24 non-H atoms is 5·7 Å^2, while it is 4·6 Å^2 for the 24 C atoms in TPHBEN. The $\langle B_{eq}\rangle$ values taken over the 12 C atoms at the *ortho* and *meta* positions of the phenyl rings, which should be especially affected by internal torsions (see below), are 6·1 Å^2 for TPHBRX and 5·0 Å^2 for TPHBEN. These differences cannot, however, be attributed to 'looser' crystal packing in TPHBRX. The molecular volume (*V*/*Z*) is 0·5% smaller for TPHBRX than for TPHBEN, even though the boron-containing molecule is just slightly larger than its hydrocarbon analogue (see Table 3). The rather large displacement parameters in TPHBRX partially account for the very poor scattering properties of the crystals; only 73 of the 758 'observed' reflections have $2\theta(\text{Mo } K\alpha) > 40°$. The displacement ellipsoids are sufficiently regular, however, that we interpret them as representing large thermal motion rather than static disorder.

Descriptions of the thermal motion in TPHBRX and TPHBEN were derived using Trueblood's program *THMV*10 (Trueblood, 1978; Schomaker & Trueblood, 1984). The molecules were treated as semi-rigid bodies with three internal degrees of freedom corresponding to torsional motions about the B—C and C—C(Ph) bonds, respectively. Although a rigid-body method had been used for the crystallographic refinement of the TPHBRX structure, the resulting **T**, **L** and **S** tensors determined for the three phenyl rings are not necessarily physically meaningful since the model treated the three rings as completely independent entities and since T^{33} was fixed arbitrarily (see above). The parameters of the **TLS** model could, however, be used to calculate atomic **U** tensors for the individual C atoms, and these values, along with the **U** tensors for the B and O atoms, were used as observations to *THMV*10. Full details of the thermal-motion descriptions for both TPHBRX and TPHBEN have been deposited.*

In both structures the **TLS** model fits the observed 'thermal' parameters adequately but not well. The quality of the structure determinations may be a problem. Non-rigidity of the B_3O_3 ring may be a complicating factor, as may other types of internal motion, such as bending at the B (or C) atom of the central ring or at the attached C atom. Several conclusions, however, can be drawn. First, the eigenvalues of the **T** tensor for TPHBRX are about 30% larger than they are for TPHBEN. Second, the torsional amplitudes about the B—C bonds in TPHBRX [35 (13), 22 (12), 40 (13)$^{\circ 2}$] are somewhat greater than the corresponding amplitudes for the C—C(Ph) bonds in TPHBEN [16 (10), 20 (11), 11 (10)$^{\circ 2}$], although the difference is only at the borderline of significance. It is interesting that the estimates of the torsional amplitudes derived for TPHBRX from the crystallographic model were considerably larger [73 (5), 64 (4), 86 (5)$^{\circ 2}$]. Large-amplitude motions result from wide, shallow potential-energy wells, which often have small central maxima. If there is a small maximum of this type, then as the temperature is lowered, it might become larger than kT. A phase transition could then be expected to occur. It seems likely (see *Experimental*) that such a transition takes place in TPHBRX crystals. We suggest that it is associated with torsional displacements about the B—C bonds.

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* See previous footnote.

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Structure of a Bryonolic Acid Derivative, 3β-Hydroxy-*D:C*-friedoolean-8-en-29-oic Acid Methyl Ester

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Abstract. $C_{31}H_{50}O_3$, $M_r = 470{\cdot}7$, trigonal, $P3_121$, $a = 18{\cdot}571$ (1), $c = 14{\cdot}018$ (2) Å, $V = 4187{\cdot}0$ (6) Å^3, $Z = 6$, $D_x = 1{\cdot}120$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ(Cu $K\alpha$) = 0·54 mm^{-1}, $F(000) = 1560$, $T = 295$ K, $R = 0{\cdot}044$ for 2639 reflections. The compound was derived from bryonolic acid isolated from *Luffa cylindrica* roots (Cucurbitaceae). Rings *A*, *B* and *C* are in the chair, half-chair and half-chair conformations, respectively. The *D–E* ring adopts a chair–chair form which is considerably distorted to relieve the repulsive

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