The conformation of the 12-membered macroring in hygrophylline is essentially similar to its conformation in the hepatotoxic alkaloids, for example senecionine (Mackay & Culvenor, 1982) and anacrotine (Mackay, Sadek & Culvenor, 1984) – see Table 3. Atoms in the primary ester groups, C(9), O(10), C(11), O(22), C(12) are coplanar within ±0·07 (1) Å. One H atom at C(9) lies closer to the ester plane than the other [torsional angle H(9b)—C(9)—O(10)—C(11) −22 (6)°] as noted in senecionine and anacrotine. However, unlike the situation in the latter, in which the α-OH substituent at C(12) lies almost in the ester plane, a twisting about the C(11)—C(12) bond results in a torsional angle O(22)—C(11)—C(12)—O(23) of −20 (5)° compared with the values −3·8 (3) and −3·4 (5)° in senecionine and anacrotine respectively. Atoms C(7), O(17), C(16), O(25), C(15) in the secondary ester are coplanar within ±0·02 (1) Å [torsional angles C(7)—O(17)—C(16)—C(15) −178·3 (5) and C(7)—O(17)—C(16)—O(25) 2·5 (5)°]. The angle between the planes defined by atoms H(7), C(7), O(17) and O(17), C(16), O(25), C(15) is 1·7 (5)° so that H(7) lies within the ester plane [the H(7)···O(25) distance is 2·45 (6) Å], whereas in anacrotine and senecionine H(7) does not lie within the ester plane; the comparable interplanar angles have the respective values 34 (3) and 68 (1)°. As observed in anacrotine, the unsaturated side chain C(15)=C(20)—C(21) is in a nearly *cis* arrangement with the carbonyl group [atoms C(14), C(15), C(20), C(21), C(16) coplanar within ±0·01 (1) Å], the torsional angle C(20)—C(15)—C(16)—O(25) of 40·5 (5)° being similar to the value 46·2 (3)° in senecionine but significantly different from the value 60·6 (5)° in anacrotine in which there is a greater twist about the C(15)—C(16) bond.

The carbonyl bonds of the ester functions in hygrophylline are antiparallel as observed in other alkaloids containing the 12-membered macroring. The angle between the bonds is 26·5 (6)° compared with the values of 14·0 (5)° in anacrotine and 16·8 (3)° in senecionine. The transannular distance O(10)···O(17) of 2·966 (5) Å is shorter than the distance in anacrotine

[3·349 (6) Å] and in senecionine [3·293 (3) Å]; other close contacts within the macroring are O(10)···C(13) 2·792 (7), O(10)···C(14) 3·252 (7) and C(11)···C(14) 3·028 (8) Å. The O(23)···O(24) and O(22)···O(24) distances of 2·818 (6) and 2·701 (5) Å respectively are indicative of hydrogen bonding, but this could not be verified as the H atom of the hydroxyl substituent at C(12) was not located in the analysis.

The crystal packing is illustrated in Fig. 2. An intermolecular H bond involving the hydroxyl substituent at C(14) and the carbonyl O of the primary ester system of an adjacent molecule related by the twofold screw axis ($y = \frac{1}{4}, z = \frac{1}{2}$) links the molecules into helices along **a**. The O(24)···O(22), O(24)—H(24) and H(24)···O(22) distances are 2·738 (6), 0·66 (8) and 2·17 (6) Å and the angle O(24)—H(24)···O(22) is 145 (5)°. It is interesting to note that the N atom in the pyrrolizidine nucleus does not enter into hydrogen bonding in this crystal.

References

CROMER, D. T. & LIBERMAN, D. (1970). *J. Chem. Phys.* **53**, 1891–1898.
CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.
MACKAY, M. F. & CULVENOR, C. C. J. (1982). *Acta Cryst.* B**38**, 2754–2758.
MACKAY, M. F., SADEK, M. & CULVENOR, C. C. J. (1984). *Acta Cryst.* C**40**, 1073–1077.
RICHARDSON, M. F. & WARREN, F. L. (1943). *J. Chem. Soc.* pp. 452–454.
SCHLOSSER, F. D. & WARREN, F. L. (1965). *J. Chem. Soc.* pp. 5707–5710.
SHELDRICK, G. M. (1976). *SHELX76*. A program for crystal structure determination. Univ. of Cambridge, England.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
STOECKLI-EVANS, H. (1980). *Acta Cryst.* B**36**, 3150–3153.

Structure of the β Form of 2,4,6-Triphenyl-1,3,5-trithiane, C21H18S3

BY K. SEKIDO AND S. HIROKAWA

Department of Chemistry, The National Defense Academy, Hashirimizu, Yokosuka 239, Japan

Abstract. $M_r = 366·5$, monoclinic, $C2/c$, $a = 19·711$ (4), $b = 9·578$ (2), $c = 19·459$ (4) Å, $\beta = 92·09$ (2)°, $V = 3671·0$ Å³, $Z = 8$, $D_x = 1·326$, $D_m = 1·323$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0·7107$ Å, $\mu = 4·12$ mm⁻¹, $F(000) = 1536$, $T = 296$ K, final $R = 0·069$ for 4395 independent reflections. The trithiane ring, which

has a chair form, is approximately parallel to the *ac* plane. All three phenyl rings are in equatorial positions; two are approximately perpendicular to the trithiane ring, and the third is inclined by about 45°.

Introduction. The structures of α- and β-2,4,6-tri-methyl-1,3,5-trithiane (TTA) have been investigated by the X-ray diffraction method (Valle, Busetti & Mammi, 1969; Hirokawa, Sekido, Suzuki & Noguchi, 1974; Sekido, Ono, Noguchi & Hirokawa, 1977; Sekido, Itoh, Noguchi & Hirokawa, 1981). TTA has two stereo-isomers: in one (m.p. 399 K) all three methyl groups are in equatorial positions and in the other (m.p. 375 K) two of the three methyl groups are in equatorial positions and the third is axial. The former is designated as the β form while the latter is the α. We have determined the crystal structure of the title compound, β-TTB (m.p. 499 K), in which a phenyl group is substituted for each methyl group in β-TTA, in order to compare the results of this investigation with those of α- and β-TTA, and related compounds.

Experimental. Colorless rectangular prismatic crystals obtained by slow evaporation from an ethyl acetate solution. D_m measured by flotation in a mixture of toluene and tetrachloromethane. Crystal 0·5 × 0·3 × 1·0 mm. Rigaku AFC-III four-circle diffractometer, Mo $K\alpha$ radiation, graphite monochromator. Intensity data measured by ω–2θ scan, scan speed 4° min⁻¹ (2θ). Cell dimensions refined by least-squares method using *RSLC*-3 (*UNICS*, 1967) based on 58 reflections with $27\cdot61 \le \theta \le 29\cdot92°$. Systematic absences restricted possible space groups to either *Cc* or *C2/c*; the number of molecules in the unit cell and the statistical test of the intensity distribution favored the latter. 5835 independent reflections measured in range $+h$, $+k$, $\pm l$. Three standard reflections (200, 020, 002), intensity variation 1·5%. $\sin\theta_{max}/\lambda = 0\cdot7030$ Å⁻¹, $2\theta_{max} = 59\cdot96°$. 5707 unique reflections, $R_{int} = 0\cdot040$. 1312 unobserved reflections with $I < 2\sigma(I)$. Data corrected for Lorentz and polarization factors but not for absorption. Three S atoms located from a Patterson synthesis, all other non H-atoms fixed by three-dimensional Fourier and difference syntheses using *RSSFR*-5 (*UNICS*, 1967). Block-diagonal anisotropic least-squares refinement (*HBLS*-5, Ashida, 1979) gave $R = 0\cdot09$ on a CDC-6600 computer of Century Research Co., Tokyo. H-atom positions located from difference Fourier map; block-diagonal least-squares refinement with anisotropic temperature factors for C and S, isotropic for H atoms; $R = 0\cdot069$, $S = 2\cdot85$, in the range $4\cdot3 \le F_o \le 485\cdot1$. Unit weights. In final refinement cycle $(\Delta/\sigma)_{max} = 0\cdot11$; max. and min. peak heights in final difference electron density map 0·177 and −0·218 e Å⁻³, respectively. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. The final coordinates and thermal parameters are given in Table 1.* The structural and conformational features are shown in Fig. 1 together with the atomic numbering and the thermal-vibration ellipsoids (Johnson, 1965) scaled to 50% probability, excluding the H atoms. Intramolecular interatomic distances and angles are given in Table 2. The average S—C length is 1·821 Å; the C—S—C and S—C—S angles are 99·5 and 114·1°, respectively. The mean values reported for the related compounds are as follows: 1·814° for S—C, 98·9° for C—S—C, and 114·7° for S—C—S in the unsubstituted 1,3,5-trithiane (Valle, Busetti, Mammi & Carazzolov, 1969), 1·818 Å, 101·3, 113·5° in β-TTA (Sekido *et al.*, 1981), and 1·818 Å, 101·89, 113·09° in α-TTA (Sekido *et al.*, 1977). The data on β-TTA by Valle, Busetti & Mammi (1969) and Hirokawa *et al.* (1974) are not discussed here. The S—C lengths in this investigation are slightly longer than those in the others, while the C—S—C angles are smaller and the S—C—S angles larger than those in TTA. These may suggest that the trithiane ring is distorted by the side-chain radicals. The mean C(*i*)—C(*i*1) bond distance (from C in the trithiane ring to a phenyl C, $i = 1$–3) and S(*i*)—C(*i*)—C(*i*1) angle are 1·514 Å and 108·8°, being in accordance with the reported values (1·519 Å and 107·6° in α-TTA, and 1·513 Å and 107·6° in β-TTA). Therefore, the C—C bond distance and S—C—C angle are rigid, regardless of the substituted groups.

The triangle formed by the three S atoms is regular, the average length being 3·055 Å and the average apex angle 60·0° (3·029 Å and 60·0° in α-TTA, and 3·040 Å and 60·0° in β-TTA). Another triangle formed by the three C atoms of the trithiane ring is also regular, with a length of 2·778 Å (2·833 and 2·812 Å in α- and β-TTA) and with the apex angle 60·0° (60·0° in α- and β-TTA). It may be characteristic that the S⋯S length is longer than the reported values, while the C⋯C length is shorter.

Intramolecular distances and angles of the phenyl rings are also given in Table 2. The average C(*ij*)—C(*ik*) bond distances and the C(*ij*)—C(*ik*)—C(*i*1) angles in the phenyl rings ($i = 1,3$) are 1·380, 1·383, 1·378 Å, respectively, and 120·0° in all the phenyl rings. Every angle for $k = 1$ and $k = 6$ is less than 120·0°. This tendency is also seen in 2,4,6-triphenylverdazyl (Williams, 1973), oxobis[triphenylgermanium(IV)] (Glidewell & Liles, 1978*a*), and hydroxotriphenyl-tin(IV) (Glidewell & Liles, 1978*b*).

Shifts of the three S atoms [S(1), S(2), S(3)] and the three C atoms [C(11), C(21), C(31)] from the least-

squares plane defined by the three C atoms of the trithiane ring are 0·68, 0·66, 0·70, 0·33, 0·30, 0·20 Å, respectively. Hence, the plane formed by these C atoms lies between the plane formed by the S atoms and the plane formed by the C atoms of the trithiane ring. Each phenyl ring is planar within experimental errors. The dihedral angle between a phenyl ring and the trithiane ring is 97° for C(1j), 87° for C(2j), and 46° for C(3j).

The absolute average value of the endocyclic torsion angles is 66·5°, being larger than 64·9° (α-TTA) and 65·0° (β-TTA). The calculated exocyclic torsion angles (171·8° as a mean in absolute values) show that all the phenyl groups are in equatorial positions. This mean value is less than the 174·4° in β-TTA and the 175·2° for C—C_{eq} in α-TTA.

Table 2. Intramolecular distances (Å) and angles (°)

S(1)–C(1)	1·825 (4)	C(1)–S(1)–C(3)	99·4 (2)
S(1)–C(3)	1·806 (3)	C(1)–S(2)–C(2)	100·0 (2)
S(2)–C(1)	1·821 (3)	C(2)–S(3)–C(3)	99·0 (2)
S(2)–C(2)	1·816 (3)	S(1)–C(1)–S(2)	114·6 (2)
S(3)–C(2)	1·826 (3)	S(2)–C(2)–S(3)	113·9 (2)
S(3)–C(3)	1·829 (3)	S(1)–C(3)–S(3)	113·8 (2)
C(1)–C(11)	1·504 (5)	S(1)–C(1)–C(11)	107·1 (2)
C(2)–C(21)	1·509 (5)	S(2)–C(1)–C(11)	109·1 (2)
C(3)–C(31)	1·530 (5)	S(2)–C(2)–C(21)	108·4 (2)
		S(3)–C(2)–C(21)	108·5 (2)
S(1)···S(2)	3·068 (1)	S(1)–C(3)–C(31)	111·8 (2)
S(1)···S(3)	3·045 (2)	S(3)–C(3)–C(31)	108·0 (2)
S(2)···S(3)	3·051 (1)		
C(1)···C(2)	2·785 (5)	S(2)···S(1)···S(3)	59·9 (1)
C(1)···C(3)	2·768 (5)	S(1)···S(2)···S(3)	59·7 (1)
C(2)···C(3)	2·780 (5)	S(1)···S(3)···S(2)	60·4 (1)
S(1)···C(11)	2·683 (3)	C(2)···C(1)···C(3)	60·1 (2)
S(1)···C(31)	2·765 (3)	C(1)···C(2)···C(3)	59·7 (2)
S(2)···C(11)	2·715 (4)	C(1)···C(3)···C(2)	60·3 (2)
S(2)···C(21)	2·704 (4)		
S(3)···C(21)	2·713 (3)		
S(3)···C(31)	2·723 (4)		

Distances and angles within the phenyl rings

	Ring, i		
	1	2	3
Bond C(ij)–C(ik)			
1–2	1·381 (5)	1·388 (6)	1·376 (5)
2–3	1·378 (5)	1·392 (6)	1·392 (6)
3–4	1·373 (7)	1·374 (6)	1·361 (7)
4–5	1·370 (7)	1·373 (7)	1·350 (7)
5–6	1·383 (6)	1·394 (6)	1·403 (6)
6–1	1·395 (6)	1·377 (5)	1·384 (6)
Bond C(ij)–H(ij)			
2	1·02 (4)	0·97 (4)	0·93 (4)
3	0·98 (4)	1·00 (4)	0·93 (4)
4	0·97 (4)	0·97 (4)	0·94 (5)
5	0·96 (4)	1·00 (4)	0·96 (5)
6	0·96 (4)	1·04 (4)	0·94 (4)
Angle C(ij)–C(ik)–C(il)			
6–1–2	119·1 (3)	119·7 (3)	119·5 (4)
1–2–3	120·2 (4)	120·6 (4)	120·1 (4)
2–3–4	120·5 (4)	119·4 (4)	120·0 (4)
3–4–5	119·9 (4)	120·2 (4)	120·8 (4)
4–5–6	120·3 (4)	120·9 (4)	120·3 (5)
5–6–1	119·9 (4)	119·3 (4)	119·3 (4)

Table 1. Atomic coordinates (×10⁴) and equivalent isotropic temperature factors

$$B_{eq} = \tfrac{4}{3}\sum_i\sum_j B_{ij}a^*_i a^*_j \mathbf{a}_i\cdot\mathbf{a}_j.$$

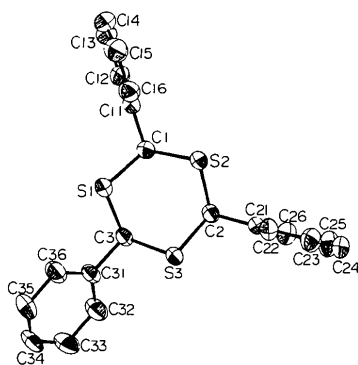|	x	y	z	B_{eq}(Å²)
S(1)	1462 (9)	3218 (10)	2322 (9)	4·38
S(2)	2968 (9)	3417 (10)	1987 (8)	2·90
S(3)	2545 (9)	3259 (10)	3478 (8)	2·94
C(1)	2141 (33)	2652 (37)	1773 (32)	2·75
C(2)	3130 (32)	2663 (36)	2833 (32)	2·63
C(3)	1764 (32)	2464 (35)	3126 (32)	2·49
C(11)	1931 (33)	3040 (37)	1048 (32)	2·74
C(12)	1764 (37)	2006 (42)	577 (37)	3·50
C(13)	1569 (41)	2351 (51)	−89 (39)	4·28
C(14)	1551 (43)	3721 (56)	−296 (40)	4·78
C(15)	1710 (47)	4759 (49)	167 (44)	4·45
C(16)	1903 (41)	4432 (43)	839 (39)	3·67
C(21)	3843 (32)	3041 (37)	3072 (31)	2·70
C(22)	4033 (37)	4432 (42)	3140 (40)	3·52
C(23)	4691 (43)	4789 (47)	3355 (44)	4·28
C(24)	5156 (28)	3749 (54)	3499 (41)	4·48
C(25)	4969 (42)	2373 (51)	3435 (47)	4·76
C(26)	4309 (39)	2006 (44)	3225 (40)	3·85
C(31)	1229 (34)	2549 (37)	3675 (33)	2·71
C(32)	1298 (42)	1690 (47)	4240 (40)	3·82
C(33)	822 (49)	1735 (56)	4750 (43)	4·80
C(34)	280 (45)	2614 (62)	4685 (44)	4·94
C(35)	204 (44)	3465 (59)	4135 (47)	4·87
C(36)	681 (41)	3449 (48)	3612 (41)	3·93

Fig. 1. The thermal-vibration ellipsoids of the non-hydrogen atoms drawn by ORTEP (Johnson, 1965).

The molecular packing in the unit cell together with intermolecular distances less than 3·81 Å are shown in Fig. 2. These distances are between two phenyl rings which are related to each other by a center of symmetry (at $x = \frac{1}{4}$, $\frac{3}{4}$) and between another two rings which are related by a twofold axis. Other distances less than 3·81 Å are 3·71 Å for C(25ⁱ)···C(34ᵛⁱ), and 3·76 Å for C(13ᵛⁱⁱ)···C(34ᵛⁱ). The interplanar distance is 3·41 Å for phenyl rings which are related to each other by a center of symmetry, and 3·56 Å for those related by a twofold axis. Hence, the molecules are held together by van der Waals contacts and by plane-to-plane interactions in the crystal. Also, these interactions may be regarded as the cause of the high melting point of this compound.
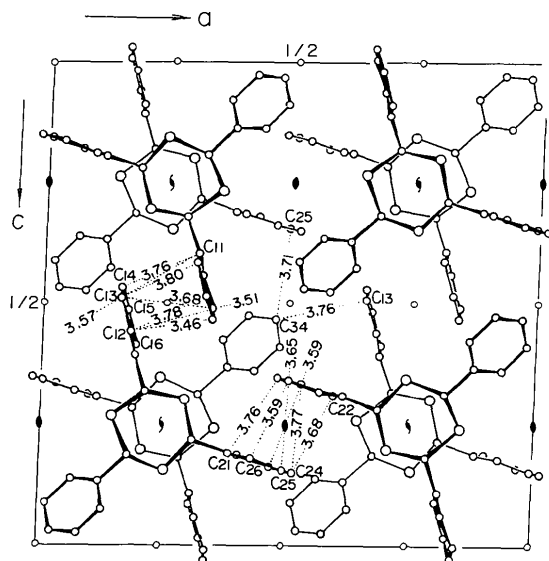
Fig. 2. The molecular packing viewed down **b**, showing all intermolecular distances (involving non-hydrogen atoms) less than 3·81 Å. Each e.s.d. is no greater than 0·01 Å.

References

ASHIDA, T. (1979). *HBLS-V*. In *The Universal Crystallographic Computing System—Osaka*, pp. 53–59. The Computation Center, Osaka Univ.

GLIDEWELL, C. & LILES, D. C. (1978a). *Acta Cryst.* B34, 119–124.

GLIDEWELL, C. & LILES, D. C. (1978b). *Acta Cryst.* B34, 129–134.

HIROKAWA, S., SEKIDO, K., SUZUKI, A. & NOGUCHI, T. (1974). *Mem. Def. Acad. Math. Phys. Chem. Eng. Yokosuka Jpn*, 14, 89–103.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.

JOHNSON, C. K. (1965). *ORTEP*. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee.

SEKIDO, K., ITOH, J., NOGUCHI, T. & HIROKAWA, S. (1981). *Bull. Chem. Soc. Jpn*, 54, 1881–1882; *Mem. Def. Acad. Math. Phys. Chem. Eng. Yokosuka, Jpn*, 21, 137–153.

SEKIDO, K., ONO, H., NOGUCHI, T. & HIROKAWA, S. (1977). *Bull. Chem. Soc. Jpn*, 50, 3149–3152.

UNICS (1967). Edited by T. SAKURAI. *RSLC*-3 and *RSSFR*-5. The Crystallographic Society of Japan.

VALLE, G., BUSETTI, V. & MAMMI, M. (1969). *Acta Cryst.* B25, 1631–1639.

VALLE, G., BUSETTI, V., MAMMI, M. & CARAZZOLOV, G. (1969). *Acta Cryst.* B25, 1432–1436.

WILLIAMS, D. E. (1973). *Acta Cryst.* B29, 96–102.

Structure of N-[1'-(9-Adenyl)-β-D-ribofuranuronosyl]-L-phenylalanine Water Ethanol (1/½/¼), $C_{19}H_{20}N_6O_6 \cdot \frac{1}{2}H_2O \cdot \frac{1}{4}C_2H_6O$

BY FUSAO TAKUSAGAWA, HELEN M. BERMAN* AND MICHAEL DABROW

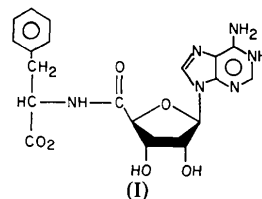*The Institute for Cancer Research, Philadelphia, Pennsylvania 19111, USA*

AND ROLAND K. ROBINS

Cancer Research Center, Brigham Young University, Provo, Utah 84602, USA

Abstract. $M_r = 448 \cdot 94$, monoclinic, $P2_1$, $a = 9 \cdot 207$ (1), $b = 10 \cdot 503$ (2), $c = 22 \cdot 208$ (3) Å, $\beta = 101 \cdot 4$ (1)°, $V = 2105 \cdot 2$ (9) Å³, $Z = 4$, $D_x = 1 \cdot 416$ g cm⁻³, λ(Cu $K\alpha$) $= 1 \cdot 5418$ Å, $\mu = 9 \cdot 3$ cm⁻¹, $F(000) = 942$, $T = 293$ K. Final $R = 0 \cdot 053$ for 4132 observed intensities. Both independent molecules in the asymmetric unit are zwitterions. One molecule has an extended conformation with the base *anti* and the sugar C(2') *endo* (^2E); the other molecule has a closed conformation with the base *syn* and the sugar C(3') *endo* (^3E).

Introduction. Nucleoside peptides are found in a variety of biological systems. *S*-Adenosylmethionine, the cofactor responsible for methylation, is one example, as are a wide variety of nucleoside antibiotics (Suhadolnik, 1970). Amino acids were first shown to bind covalently to RNA in 1958 (Akashi & Yokoi, 1958). Covalent

protein–nucleic acid attachments have been demonstrated in adenovirus (Rekosh, Russell, Bellet & Robinson, 1977) and polyovirus (Rothberg, Harris, Nomoto & Wimmer, 1978). As one method to aid in the identification of nucleoside peptides in DNA and RNA, model compounds have been synthesized (Robins *et al.*, 1971). The crystal structure of one, N-[1'-(9-adenyl)-β-D-ribofuranuronosyl]-L-phenylalanine (I) (Kawana, Rousseau & Robins, 1972), has been determined as part of our program to understand the detailed geometry of these molecules as well as their intermolecular interactions.

(I)