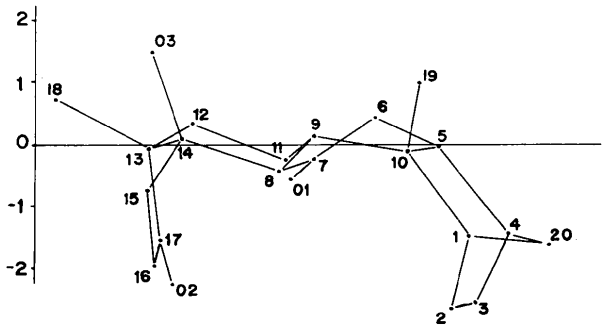

Fig. 5. A view of the overall conformation of the steroid. The molecule is viewed parallel to the least-squares mean plane through rings *B* and *C* and perpendicular to the C(8)–C(14) bond. The scale is in ångstrom units.

It is usual to define a least-squares mean plane through the atoms C(5)–C(7) as a reference element for the gross analysis of steroid conformations (Duax *et al.*, 1976). However, owing to the *cis* junctions of rings *A*/*B* and *C*/*D*, rings *A* and *D* are significantly folded towards each other on the α face to give a compact molecule. In fact, mean planes through rings *A* and *D* make angles of *ca* 84 and 117°, respectively, with the mean plane through rings *B* and *C* (Fig. 5). Likewise the twist about the length of the molecule is defined using the torsion angle C(19)–C(10)···C(13)–C(18), which has a value of 36·9 (2)° in the present molecule. This value is considerably smaller than those obtained when ring *B* has 8β sofa or 7α,8β half-chair conformations (Duax *et al.*, 1976).

The longer bonds in the molecule (Fig. 2) involve atoms with attached H atoms and/or substituents approximately eclipsed. The crystal packing is determined by hydrogen bonds involving the 14β-hydroxy group [O(1)···H(1) $(-x, 1-y, 1-z) = 2{\cdot}00$ (2) Å, O(1)···H(1)–O(3) = 164 (1)°, C(7)–O(1)···H(1) = 97·3 (4)°]. Other short intramolecular O···H contacts are O(1)···H(61) = 2·39 (1) and O(3)···H(181) = 2·48 (2) Å.

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Structure of Sperminium Tetranitrate*†

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Abstract. 1,5,10,14-Tetraazoniatetradecane tetranitrate, $C_{10}H_{30}N_4^{4+}.4NO_3^-$, $M_r = 454{\cdot}4$, monoclinic, $P2_1/c$, $a = 9{\cdot}593$ (1), $b = 8{\cdot}4623$ (7), $c = 13{\cdot}314$ (2) Å, $\beta = 91{\cdot}38$ (1)°, $V = 1080{\cdot}5$ (2) Å^3, $Z = 2$, $D_x = 1{\cdot}396$ Mg m^{-3}, λ(Cu $K\alpha$) = 1·54178 Å, $\mu = 1{\cdot}00$ mm^{-1}, $F(000) = 484$, $T = 290$ K, $R = 0{\cdot}057$ for 1241 observed reflexions. The centrosymmetric sperminium tetracation adopts a generally stretched form with all bonds *trans* except for the terminal N–C–C–C torsion angles which are *gauche*. One nitrate anion forms H bonds only with secondary $-NH_2^+-$ ammonium groups while the other accepts H bonds exclusively from primary $-NH_3^+$ groups. Each

* Studies of Biogenic Polyamines. II.

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NO_3^- anion uses only one of its O atoms to form (two) relatively strong H bonds. The corresponding N—O bonds are longer [1·264 (2) *vs* 1·215 (3) Å] and form smaller O—N—O angles [118·5 (4) *vs* 123·0 (1)°].

Introduction. Putrescine, spermidine and spermine are aliphatic biogenic polyamines known to be important factors in various biological processes. Particularly important is their stabilizing effect on secondary and tertiary structures of nucleic acids. These amines are strong bases and in biological systems exist as polycations which, by interacting with nucleic-acid polyanions, can influence their conformations. So far, a number of crystal structures of biogenic polyamine salts have been determined to study conformational and H-bonding properties of these organic polycations. Most of them were putrescinium salts whereas spermidine and spermine have been studied only as chloride (Giglio, Liquori, Puliti & Ripamonti, 1966*a*,*b*) and hydrated hydrogenphosphate (Huse & Iitaka, 1969; Iitaka & Huse, 1965) salts. In the case of the putrescinium dication it was concluded that, in spite of its marked flexibility (*trans* and *gauche* conformations occurring with equal frequency), it shows a strong tendency to be centrosymmetric and that there is no uniform way in which the $-NH_3^+$ ammonium groups would enter into H bonding (Jaskólski, Alejska & Wiewiórowski, 1986; Jaskólski, 1987). The sperminium tetracation is another symmetrical system and it was of interest to verify if the above conclusions are also valid here. The chloride and hydrogenphosphate salts of sperminium (Giglio, Liquori, Puliti & Ripamonti, 1966*b*; Iitaka & Huse, 1965) suggest a positive answer but, since further data are still necessary, the present structure determination of sperminium tetranitrate has been undertaken.

Experimental. Suitable crystals from ethanol/water solution. Crystal 0·2 × 0·3 × 0·35 mm, Syntex $P2_1$ diffractometer, graphite monochromator, Cu $K\alpha$ radiation. Cell parameters from least-squares treatment of setting angles of 15 reflexions ($23 \le 2\theta \le 30°$). θ:2θ profiles measured for 1495 unique $+h+k\pm l$ reflexions with $2\theta \le 115°$ [$(\sin\theta)/\lambda_{max} = 0{\cdot}547$ Å^{-1}; $0 \le h \le 10$, $0 \le k \le 9$, $-14 \le l \le 14$], profile analysis according to Lehmann & Larsen (1974). No significant intensity variation (<2%) for two standard reflexions measured every 1·5 h. No absorption or extinction corrections. 1241 observed reflexions with $I \ge 1{\cdot}96\sigma(I)$. Structure solved by direct methods using *SHELX*76 (Sheldrick, 1976). Full-matrix least-squares refinement on F, unit weights. Anisotropic non-H atoms; H atoms at C(2), C(3), C(4) and C(6) generated geometrically and riding on their C atoms, all C—H hydrogen atoms given common (refinable) B_{iso}, N—H hydrogen atoms as well as H(71) and H(72) located from a ΔF map and included in the refinement (N—H hydrogen atoms with individual isotropic temperature factors). Final convergence: $R = 0{\cdot}057$, $wR = 0{\cdot}049$, $S = 0{\cdot}85$, $(\Delta/\sigma)_{max} = 0{\cdot}29$, largest peak in final ΔF map = 0·32 e Å^{-3}, largest trough = −0·20 e Å^{-3}. Computer programs: *SHELX*76 and local programs (Jaskólski, 1982*a*), molecular illustrations drawn using *PLUTO* (Motherwell & Clegg, 1978) and *ORTEP* (Johnson, 1976). Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Atomic coordinates are listed in Table 1.* The geometry of the ions is characterized in Table 2 and a thermal-ellipsoid representation of the sperminium tetracation is shown in Fig. 1. The cation is located on an inversion centre and therefore retains its potential symmetry. It adopts a generally stretched form with all bonds *trans* except for the terminal N—C—C—C torsion angles which are *gauche*. In sperminium hydrogenphosphate hexahydrate the sperminium tetracation was found to adopt the all-*trans* zigzag conformation (Iitaka & Huse, 1965) while in sperminium tetrachloride it adopted a partly folded conformation with *gauche* turns at the C(6)—N(5) bonds (Giglio, Liquori, Puliti & Ripamonti, 1966*a*). The bond angles along the polycation chain [average 112·3 (4)°] are slightly larger than the tetrahedral value. In contrast to the observation by Giglio, Liquori, Puliti & Ripamonti (1966*a*), the valence angles at the bond in the *gauche* conformation show no appreciable widening with respect to the remaining angles. The two independent nitrate ions show significant and similar deviations from trigonal symmetry. These deviations can be interpreted in terms of the (similar) H bonds formed by the anions (see below): the N—O bonds for oxygen atoms engaged in strong H bonds [O(11) in N(10)-nitrate and O(21) in N(20)-nitrate] are elongated [1·264 (2) *vs* 1·215 (3) Å] and form smaller O—N—O angles [118·5 (4) *vs* 123·0 (1)°]. The N(10)-nitrate anion is nearly planar [$\chi^2 = 11{\cdot}0$, N 0·013 (3) Å above the O···O···O plane] while the N(20)-nitrate ion shows slight but significant deviations from planarity [$\chi^2 = 41{\cdot}7$, N 0·025 (3) Å above the O···O···O plane]. The N(20)-nitrate anion is located close to the $-NH_3^+$ group of the cation and forms three H bonds [two stronger bonds at the O(21) centre and a weak bond at the O(22) centre] with the $-NH_3^+$ terminal of three different cations. The other NO_3^- anion is located near the $-NH_2^+-$ group and forms two relatively strong H bonds [at the O(11) centre] with the $-NH_2^+-$ groups on two different cations (Table 3). In consequence, from the point of view of H bonding, each of the ammonium

* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43838 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

centres on the cation is associated with 'its own' NO_3^- anion (Fig. 2). The ΔHA parameters* (Jaskólski, 1982*b*) in Table 3 suggest that the H bonds to the secondary N atom are stronger than those involving the terminal $-NH_3^+$ ammonium group. Woo, Seemen & Rich (1979) suggested that in the case of a putrescinium cation the electron-rich H-bond acceptors surrounding the $-NH_3^+$ group should be arranged on an equilateral triangle. However, that hypothesis was not confirmed by subsequent structures of putrescinium salts (Jaskólski, Alejska & Wiewiórowski, 1986; Jaskólski, 1987). Also, the three O atoms H-bonded to the $-NH_3^+$ group of the present sperminium cation form a fairly irregular triangle [edges 4·761 (4), 5·615 (4), 6·387 (5) Å]. The two H-bond acceptors at $-NH_2^+-$ are 4·682 (4) Å apart. There are two short C—H···O contacts in the structures (Table 3). They both involve C—H donors adjacent to positively charged N atoms and according to Taylor & Kennard (1982) could therefore be classified as C—H···*A* hydrogen bonds.

* ΔHA describes the shortening of the hydrogen···acceptor distance (d_{HA}) in an H bond with respect to the sum of the corresponding van der Waals radii ($r_H + r_A$). The shortening ($r_H + r_A - d_{HA}$) is expressed as a fraction of ($r_H + r_A$): $\Delta HA = 100(r_H + r_A - d_{HA})/(r_H + r_A)$.

Table 1. *Final fractional coordinates and equivalent isotropic thermal parameters* (Å²)

$U_{eq} = (U_{11}\,U_{22}\,U_{33})^{1/3}$.

	x	*y*	*z*	U_{eq}
N(1)	0·5207 (4)	0·2607 (5)	0·3730 (3)	0·048 (1)
C(2)	0·4015 (4)	0·3453 (5)	0·4189 (3)	0·047 (1)
C(3)	0·2665 (4)	0·3197 (5)	0·3607 (2)	0·045 (1)
C(4)	0·2686 (3)	0·3893 (5)	0·2568 (3)	0·046 (1)
N(5)	0·1332 (3)	0·3743 (4)	0·2021 (2)	0·039 (1)
C(6)	0·1368 (4)	0·4506 (4)	0·1011 (2)	0·044 (1)
C(7)	−0·0023 (4)	0·4529 (5)	0·0488 (3)	0·047 (1)
N(10)	0·1507 (4)	−0·0298 (4)	0·1479 (2)	0·058 (1)
O(11)	0·0588 (3)	0·0545 (3)	0·1887 (2)	0·060 (1)
O(12)	0·2439 (3)	0·0366 (4)	0·1029 (2)	0·089 (1)
O(13)	0·1449 (4)	−0·1723 (4)	0·1574 (3)	0·094 (2)
N(20)	0·6072 (3)	0·3672 (4)	0·1259 (3)	0·054 (1)
O(21)	0·5870 (3)	0·4592 (3)	0·1987 (2)	0·061 (1)
O(22)	0·6357 (4)	0·4242 (5)	0·0453 (2)	0·085 (2)
O(23)	0·5901 (5)	0·2270 (4)	0·1384 (3)	0·091 (2)

Table 2. *Bond distances* (Å), *angles* (°) *and torsion angles* (°)

N(1)–C(2)	1·492 (5)	N(1)–C(2)–C(3)	112·2 (3)
C(2)–C(3)	1·508 (5)	C(2)–C(3)–C(4)	112·7 (3)
C(3)–C(4)	1·504 (5)	C(3)–C(4)–N(5)	112·9 (3)
C(4)–N(5)	1·480 (5)	C(4)–N(5)–C(6)	111·5 (3)
N(5)–C(6)	1·494 (4)	N(5)–C(6)–C(7)	112·7 (3)
C(6)–C(7)	1·491 (5)	C(6)–C(7)–C(7^i)	111·1 (4)
C(7)–C(7^i)	1·525 (8)		

N(1)–C(2)–C(3)–C(4)	−65·0 (4)	C(4)–N(5)–C(6)–C(7)	−173·7 (4)
C(2)–C(3)–C(4)–N(5)	−176·0 (43)	N(5)–C(6)–C(7)–C(7^i)	173·9 (4)
C(3)–C(4)–N(5)–C(6)	177·5 (3)	C(6)–C(7)–C(7^i)–C(6^i)	180·0*

Symmetry code: (i) $-x, 1-y, -z$.

* Fixed by symmetry.

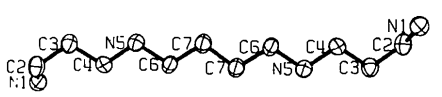

Fig. 1. Thermal-ellipsoid perspective view of the sperminium tetracation. H atoms are not shown.

Table 3. *Parameters characterizing the* H *bonds*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*	ΔHA*
N(1)–H(11)···O(22^{ii})	0·91 (5) Å	2·30 (5) Å	2·967 (5) Å	130 (3)°	7·1
N(1)–H(12)···O(21^{iii})	1·02 (5)	1·90 (5)	2·906 (5)	170 (3)	21·0
N(1)–H(13)···O(21)	0·81 (6)	2·16 (6)	2·947 (5)	163 (4)	18·2
N(5)–H(51)···O(11^{iv})	0·76 (4)	2·07 (4)	2·821 (4)	175 (3)	24·8
N(5)–H(52)···O(11)	0·97 (4)	1·85 (4)	2·803 (4)	170 (2)	25·3
C(2)–H(22)···O(23^v)	1·08	2·31	3·321 (5)	154	3·8
C(6)–H(62)···O(13^{vi})	1·08	2·28	3·278 (5)	153	5·1

Symmetry codes: (ii) $x, 0.5-y, 0.5+z$; (iii) $1-x, y-0.5, 0.5-z$; (iv) $-x, 0.5+y, 0.5-z$; (v) $1-x, 0.5+y, 0.5-z$; (vi) $x, 1+y, z$.

* Jaskólski (1982*b*).

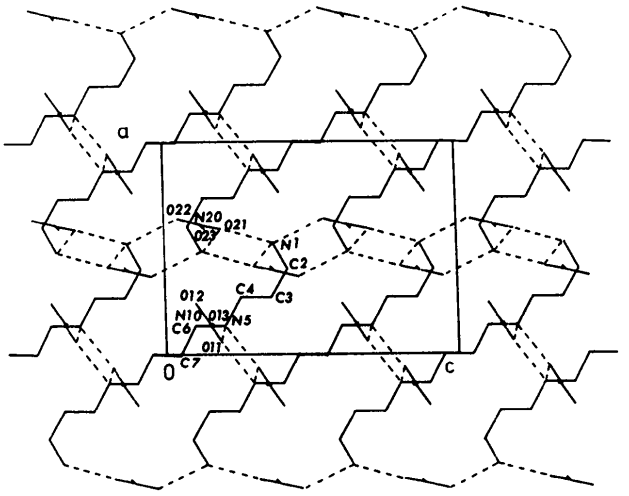

Fig. 2. Crystal packing viewed along **b**. N—H···O hydrogen bonds are indicated by broken lines.

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Structure of Taxusin

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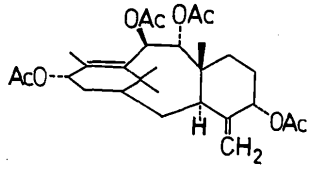
Abstract. Taxa-4(20),11-diene-5α,9α,10β,13α-tetraol tetraacetate–pentane (1/1). $C_{28}H_{40}O_8.C_5H_{12}$, M_r = 576·77, orthorhombic, $P2_12_12_1$, a = 8·032 (6), b = 17·483 (3), c = 23·066 (4) Å, V = 3238·89 Å^3, Z = 4, D_x = 1·183 g cm^{-3}, λ(Mo $K\alpha$) = 0·7093 Å, μ(Mo $K\alpha$) = 0·72 cm^{-1}, $F(000)$ = 1256, T = 298 K, R = 0·057 for 1826 reflections. Taxusin was isolated from the heartwood of *Taxus mairei* and the structure reveals the bicyclo[5.3.1]undecane skeleton with a cyclohexane ring fused at the C3 and C8 positions. The olefinic centers in the skeleton indicate both rigid *trans*-cyclodecene and *exo*-methylene geometry in a highly oxygenated environment.

Introduction. Taxusin has been isolated from the heartwood of yew (*Taxus baccata* L.) (De Marcano & Halsall, 1969). Circular dichroism, optical rotatory dispersion (De Marcano & Halsall, 1970) and ^{13}C NMR (De Marcano, Mendez, De Mendez, Monasterios, Rojas & Halsall, 1983) studies on the structure of taxusin have been performed. The structure below was proposed.



We have isolated taxusin from the heartwood of *Taxus mairei*. Its NMR, IR data and m.p. are identical with the reported values (De Marcano & Halsall, 1969). However, the specific rotation of taxusin $[\alpha]_D^{24°C}$ = 95° (c = 1, MeOH) is slightly different from the literature value of [α] = 111° (De Marcano & Halsall, 1969). A single crystal of taxusin was prepared and an X-ray diffraction study carried out to confirm the structure.

Experimental. *Taxus mairei* was collected from Yi-lan, Taiwan, and was extracted with methanol. The *n*-hexane-soluble part was subjected to column chromatography to afford taxusin, m.p. = 397–399 K (lit. 399 K) and several other taxane derivatives. Single crystals of taxusin were grown from pentane at room temperature.

A colorless crystal of dimensions 0·30 × 0·35 × 0·45 mm was used for data collection. CAD-4 diffractometer, graphite-monochromated Mo $K\alpha$ radiation. Unit-cell dimensions determined from a least-squares refinement of 25 reflections (21·0 < 2θ < 30·8°). Intensity data for 2θ < 60° were collected at variable scan speed (20/15)–(20/3)° min^{-1} by use of the $\omega/2\theta$ scan technique, with a scan range 0·7° + 0·35 tanθ; h 0→11, k 0→24, l 0→32. Three reflections monitored every 2 h, fluctuation within 2%. No correction for absorption, 5267 unique reflections were collected, 1826 observed reflections with $I > 2\sigma(I)$.

The structure was solved by direct methods using *MULTAN* with 244 largest E values, 100 smallest E values and 2890 $\sum_2$ phase relationships. All non-

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