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Structure of Taxusin

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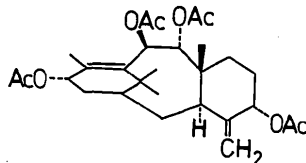
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Abstract. Taxa-4(20),11-diene-5 α ,9 α ,10 β ,13 α -tetraol tetraacetate–pentane (1/1). $C_{28}H_{40}O_8 \cdot C_5H_{12}$, $M_r = 576.77$, orthorhombic, $P2_12_12_1$, $a = 8.032$ (6), $b = 17.483$ (3), $c = 23.066$ (4) Å, $V = 3238.89$ Å³, $Z = 4$, $D_x = 1.183$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.7093$ Å, $\mu(\text{Mo } K\alpha) = 0.72$ 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 Marciano & Halsall, 1969). Circular dichroism, optical rotatory dispersion (De Marciano & Halsall, 1970) and ¹³C NMR (De Marciano, 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 Marciano & Halsall, 1969). However, the specific rotation of taxusin $[\alpha]_D^{24^\circ} = 95^\circ$ ($c = 1$, MeOH) is slightly different from the literature value of $[\alpha] = 111^\circ$ (De Marciano & 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 ($21.0 < 2\theta < 30.8^\circ$). Intensity data for $2\theta < 60^\circ$ 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 $0.7^\circ + 0.35 \tan \theta$; $h 0 \rightarrow 11$, $k 0 \rightarrow 24$, $l 0 \rightarrow 32$. 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 Σ_2 phase relationships. All non-

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Table 1. Atomic parameters and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{\text{eq}} = (\frac{8}{3}\pi^2) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
C1	0.3932 (9)	0.2499 (4)	0.1837 (3)	4.4 (4)
C2	0.3584 (9)	0.3386 (4)	0.1890 (3)	4.6 (4)
C3	0.2072 (9)	0.3651 (4)	0.2257 (3)	4.0 (4)
C4	0.2523 (10)	0.4284 (4)	0.2682 (3)	4.8 (5)
C5	0.1168 (10)	0.4457 (4)	0.3118 (3)	5.2 (5)
C6	-0.0466 (10)	0.4631 (4)	0.2833 (3)	5.5 (5)
C7	-0.0923 (10)	0.4051 (4)	0.2366 (3)	4.6 (4)
C8	0.0483 (9)	0.3919 (4)	0.1921 (3)	4.4 (4)
C9	-0.0124 (9)	0.3361 (4)	0.1448 (3)	4.0 (4)
C10	-0.0487 (9)	0.2521 (4)	0.1605 (3)	3.5 (4)
C11	0.1029 (9)	0.2123 (4)	0.1833 (3)	3.5 (4)
C12	0.1070 (9)	0.1884 (3)	0.2392 (3)	3.7 (4)
C13	0.2677 (10)	0.1649 (4)	0.2651 (3)	4.6 (4)
C14	0.4170 (10)	0.2134 (5)	0.2436 (3)	5.4 (4)
C15	0.3846 (11)	0.4721 (4)	0.2675 (3)	6.1 (5)
C16	0.2658 (9)	0.2061 (4)	0.1484 (3)	4.2 (4)
C17	0.2663 (11)	0.2371 (4)	0.0846 (3)	5.2 (5)
C18	0.3147 (10)	0.1200 (4)	0.1408 (3)	4.9 (4)
C19	0.0823 (11)	0.4676 (4)	0.1598 (3)	5.3 (5)
C20	-0.0451 (9)	0.1852 (4)	0.2783 (3)	4.5 (4)
C21	0.0418 (11)	0.3846 (5)	0.4011 (3)	6.0 (5)
C22	0.0319 (14)	0.3098 (5)	0.4306 (4)	7.7 (7)
C23	-0.1866 (11)	0.3857 (4)	0.0680 (3)	5.3 (5)
C24	-0.3574 (11)	0.4072 (5)	0.0521 (3)	6.3 (5)
C25	-0.1968 (9)	0.1553 (4)	0.1104 (3)	4.2 (4)
C26	-0.2340 (11)	0.1224 (4)	0.0517 (3)	6.2 (6)
C27	0.3139 (11)	0.1163 (5)	0.3600 (3)	6.2 (5)
C28	0.3057 (13)	0.1363 (6)	0.4239 (4)	8.0 (7)
O1	0.1003 (7)	0.3765 (3)	0.3470 (2)	5.2 (3)
O2	0.0010 (9)	0.4451 (4)	0.4211 (2)	8.5 (5)
O3	-0.1730 (6)	0.3633 (3)	0.1233 (2)	4.4 (2)
O4	-0.0682 (7)	0.3859 (3)	0.0353 (2)	6.9 (4)
O5	-0.1006 (6)	0.2175 (3)	0.1057 (2)	4.5 (3)
O6	-0.2485 (6)	0.1311 (3)	0.1552 (2)	5.3 (3)
O7	0.2594 (8)	0.1739 (3)	0.3276 (2)	5.9 (4)
O8	0.3640 (11)	0.0584 (4)	0.3412 (2)	11.1 (7)
C29	1.0668 (15)	0.1518 (9)	0.6089 (5)	13.8 (14)
C30	1.0109 (16)	0.0966 (7)	0.5648 (5)	12.4 (9)
C31	0.9307 (10)	0.1309 (4)	0.5211 (3)	5.1 (5)
C32	0.8639 (17)	0.0794 (5)	0.4860 (5)	12.0 (10)
C33	0.7874 (15)	0.1178 (6)	0.4343 (5)	11.4 (9)

hydrogen atoms located from *E* map. The positions of H atoms were calculated from an idealized geometry and checked with the *D* map. All non-hydrogen atoms were refined anisotropically and all H atoms were fixed and not refined. Final $R(F) = 5.73\%$ ($wR = 6.03\%$), weighting scheme $w = 1/[\sigma^2(F) + (0.01F)^2]$, $\Delta/\sigma < 0.2$, peak in difference map $< 0.2 \text{ e } \text{\AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations were performed using the NRCC SDP PDP-11 package (Gabe & Lee, 1981) and *MULTAN* and *ORTEPB* from the Enraf-Nonius (1979) *Structure Determination Package* on a PDP-11/23 computer.

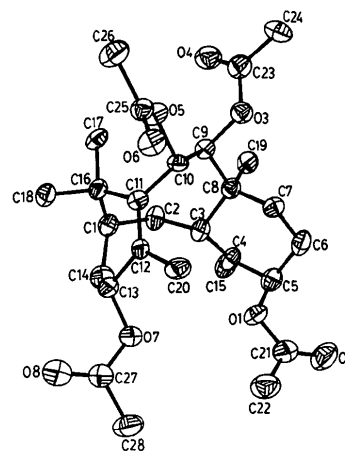
Discussion. The positional and isotropic thermal parameters are given in Table 1.* Bond lengths and angles are given in Table 2. The crystal structure contains discrete taxusin molecules and pentane molecules. C4–C15 and C11–C12, 1.31 (1) and

* 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 43801 (38 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and bond angles (°)

C1–C2	1.580 (9)	C13–C14	1.55 (1)
C2–C3	1.551 (9)	C16–C18	1.566 (9)
C4–C5	1.51 (1)	C21–O2	1.20 (1)
C5–O1	1.462 (8)	C23–O4	1.214 (9)
C8–C9	1.544 (9)	C25–O6	1.190 (8)
C9–O3	1.461 (8)	C27–O8	1.17 (1)
C11–C12	1.356 (8)	C31–C32	1.32 (1)
C12–C20	1.520 (9)	C1–C16	1.515 (9)
C16–C17	1.570 (9)	C3–C8	1.56 (1)
C21–O1	1.342 (8)	C5–C6	1.50 (1)
C23–O3	1.340 (8)	C7–C8	1.54 (1)
C25–O5	1.339 (8)	C9–C10	1.540 (9)
C27–O7	1.328 (9)	C10–O5	1.462 (7)
C30–C31	1.34 (1)	C12–C13	1.48 (1)
C1–C14	1.53 (1)	C13–O7	1.451 (7)
C3–C4	1.523 (9)	C21–C22	1.48 (1)
C4–C15	1.31 (1)	C23–C24	1.47 (1)
C6–C7	1.53 (1)	C25–C26	1.501 (9)
C8–C19	1.543 (9)	C27–C28	1.52 (1)
C10–C11	1.497 (9)	C29–C30	1.47 (1)
C11–C16	1.540 (9)	C32–C33	1.50 (1)

C2–C1–C14	111.1 (5)	C2–C1–C16	114.7 (6)
C14–C1–C16	110.9 (5)	C1–C2–C3	118.3 (5)
C2–C3–C4	112.5 (5)	C2–C3–C8	117.2 (5)
C4–C3–C8	107.2 (5)	C3–C4–C5	113.7 (5)
C3–C4–C15	127.5 (6)	C5–C4–C15	118.5 (6)
C4–C5–C6	112.3 (6)	C4–C5–O1	105.6 (5)
C6–C5–O1	109.4 (6)	C5–C6–C7	112.7 (6)
C6–C7–C8	113.1 (6)	C3–C8–C7	108.2 (5)
C3–C8–C9	114.7 (5)	C3–C8–C19	110.6 (5)
C7–C8–C9	109.4 (5)	C7–C8–C19	108.9 (5)
C9–C8–C19	104.9 (5)	C8–C9–C10	119.8 (5)
C8–C9–O3	108.2 (5)	C10–C9–O3	102.9 (5)
C9–C10–C11	111.8 (5)	C9–C10–O5	104.1 (4)
C11–C10–O5	110.1 (5)	C10–C11–C12	119.8 (6)
C10–C11–C16	122.7 (5)	C12–C11–C16	117.0 (6)
C11–C12–C13	119.4 (6)	C11–C12–C20	123.8 (6)
C13–C12–C20	116.8 (5)	C12–C13–C14	113.2 (5)
C12–C13–O7	109.3 (5)	C14–C13–O7	107.1 (5)
C1–C14–C13	114.8 (5)	C1–C16–C11	104.9 (5)
C1–C16–C17	109.1 (5)	C1–C16–C18	112.2 (6)
C11–C16–C17	117.9 (6)	C11–C16–C18	109.9 (5)
C17–C16–C18	103.1 (5)	C22–C21–O1	110.8 (6)
C22–C21–O2	126.1 (7)	O1–C21–O2	123.1 (7)
C24–C23–O3	112.9 (6)	C24–C23–O4	125.2 (6)
O3–C23–O4	121.9 (7)	C26–C25–O5	110.6 (5)
C26–C25–O6	125.2 (6)	O5–C25–O6	124.2 (5)
C28–C27–O7	110.9 (6)	C28–C27–O8	125.0 (7)
O7–C27–O8	124.1 (6)	C5–O1–C21	117.5 (5)
C9–O3–C23	119.3 (5)	C10–O5–C25	115.4 (4)
C13–O7–C27	117.4 (5)	C29–C30–C31	112.1 (1)
C30–C31–C32	110.5 (8)	C31–C32–C33	110.4 (8)

Fig. 1. The molecular structure and labeling scheme of C₂₈H₄₀O₈ (taxusin).

1.356 (8) Å respectively, are double bonds. The remaining C—C bonds in the skeleton, ranging from 1.48 (1) to 1.580 (9) Å, are all single. The four acetyl groups are normal and at 5 α , 9 α , 10 β , 13 α positions. The result confirms the structure proposed by Halsall (De Marciano & Halsall, 1969). Fig. 1 is a view of the molecule with atom numbering.

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Structure of Taiwanxan

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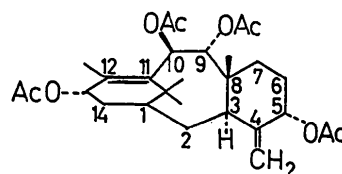
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Abstract. Taxa-4(20),11-diene-2 α ,5 α ,9 α ,10 β ,14 β -pentol 2 α ,9 α ,10 β -triacetate 14 β - α -methylbutyrate, C₃₁H₄₆O₉, M_r = 562.71, orthorhombic, $P2_12_12_1$, a = 12.036 (2), b = 12.970 (2), c = 19.550 (4) Å, V = 3051.87 Å³, Z = 4, D_x = 1.225 g cm⁻³, λ (Mo $K\alpha$) = 0.7093 Å, μ (Mo $K\alpha$) = 0.83 cm⁻¹, $F(000)$ = 1216, T = 298 K, R = 0.057 for 1057 observed reflections. Taiwanxan 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 C3 and C8 positions. The olefinic centers in the skeleton indicate both rigid *trans*-cyclodecene and *exo*-methylene geometry in a highly oxygenated environment. Taiwanxan is a hitherto unknown compound with α -methylbutyrate at C14.

Introduction. Taxusin derivatives are ubiquitous natural compounds; for example, seven new taxane derivatives have been isolated from the heartwood of yew (*Taxus baccata* L.) (De Marciano & Halsall, 1969) including taxusin (formula below). Their structures and stereochemistry were determined mainly from NMR spectroscopy. Tetrol, pentol and hexol derivatives were known (Woods, Chiang, Nakadaira & Nakanishi, 1968). We have isolated a new taxane derivative from

the heartwood of *Taxus mairei* and determined its structure by X-ray single-crystal diffraction studies.



Experimental. A colorless crystal of dimensions 0.10 × 0.35 × 0.50 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 ($20.4 < 2\theta < 25.2^\circ$). Intensity data for $2\theta < 50^\circ$ were collected at variable scan speed (20/16)–(20/3)° min⁻¹ by use of the $\omega/2\theta$ scan technique, with a scan range $0.6^\circ + 0.35\tan\theta$; h 0→14, k 0→15, l 0→23. Three reflections monitored every 2 h, fluctuation within 2%. No correction for absorption, 3020 unique reflections, 1509 observed reflections with $I > 2\sigma(I)$.

The structure was solved by direct methods using *MULTAN*. All non-hydrogen atoms located from *E* map. The positions of H atoms were calculated from an idealized geometry and checked with the *D* map. All non-hydrogen atoms were refined anisotropically and

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