

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 Marcano & Halsall, 1969). Fig. 1 is a view of the molecule with atom numbering.

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Structure of Taiwanxan

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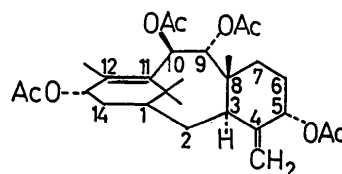
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Abstract. Taxa-4(20),11-diene-2 α ,5 α ,9 α ,10 β ,14 β -pentol 2 α ,9 α ,10 β -triacetate 14 β - α -methylbutyrate, C₃₁H₄₆O₉, M_r = 562.71, orthorhombic, $P2_12_12_1$, a = 12.036 (2), b = 12.970 (2), c = 19.550 (4) Å, V = 3051.87 Å³, Z = 4, D_x = 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 Marcano & 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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Table 1. Comparison of NMR data for compounds (I) and (II)

| p.p.m. | =CH ₂ | C2 | C5 | C7 | C9 | C10 | C8 | C12 | C15 | C15' | C3 | C14 |
|---------------|------------------|--------------|-----------------------|---------|----------|----------|------|------|------|------|---------|--------------|
| Compound (I) | 5:20 | 5:43q | 4:23bs | 5:07q | 5:84d | 6:12d | 0:86 | 2:17 | 1:74 | 1:12 | 3:34d | |
| | 4:81 | J=3.7Hz | W _{1/2} =7Hz | J=5.9Hz | J=10Hz | J=10Hz | | | | | J=7Hz | |
| Compound (II) | 5:17 | 5:04q | 4:21 | | 5:79d | 6:11d | 0:83 | 2:15 | 1:73 | 1:09 | 3:30d | 5:42q |
| | 4:77 | J=4-9, 9:2Hz | broad | | J=10:4Hz | J=10:4Hz | | | | | J=6:6Hz | J=2:3, 6:4Hz |

Table 2. Atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

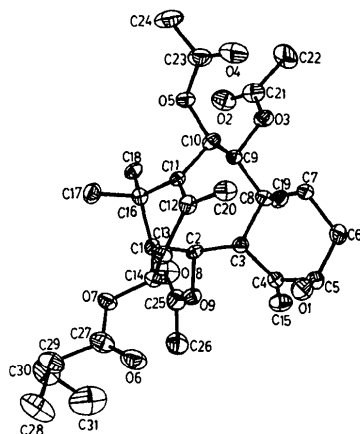
$$B_{eq} = (\frac{8}{3}\pi^2) \sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

| | x | y | z | B _{eq} (Å ²) |
|-----|--------------|--------------|------------|-----------------------------------|
| C1 | 0.3029 (6) | -0.2386 (6) | 0.2777 (4) | 2.8 (4) |
| C2 | 0.3511 (6) | -0.1293 (6) | 0.2715 (4) | 3.0 (4) |
| C3 | 0.2722 (7) | -0.0386 (6) | 0.2878 (4) | 3.1 (4) |
| C4 | 0.3135 (7) | 0.0462 (6) | 0.3353 (4) | 3.3 (5) |
| C5 | 0.2214 (8) | 0.1063 (7) | 0.3672 (4) | 3.8 (5) |
| C6 | 0.1592 (8) | 0.1599 (7) | 0.3110 (4) | 4.6 (6) |
| C7 | 0.1236 (8) | 0.0871 (6) | 0.2520 (4) | 3.8 (5) |
| C8 | 0.2231 (7) | 0.0225 (6) | 0.2239 (4) | 3.2 (4) |
| C9 | 0.1799 (7) | -0.0452 (7) | 0.1643 (4) | 3.1 (4) |
| C10 | 0.0857 (7) | -0.1232 (6) | 0.1777 (4) | 3.2 (5) |
| C11 | 0.1197 (7) | -0.2019 (6) | 0.2289 (4) | 2.7 (4) |
| C12 | 0.0704 (7) | -0.2021 (6) | 0.2910 (4) | 3.0 (4) |
| C13 | 0.1248 (8) | -0.2555 (7) | 0.3517 (4) | 3.6 (5) |
| C14 | 0.2522 (6) | -0.2561 (7) | 0.3476 (4) | 3.1 (4) |
| C15 | 0.4186 (9) | 0.0808 (8) | 0.3438 (5) | 5.2 (6) |
| C16 | 0.2240 (6) | -0.2693 (6) | 0.2188 (4) | 2.9 (4) |
| C17 | 0.1879 (8) | -0.3843 (7) | 0.2264 (4) | 4.2 (5) |
| C18 | 0.2834 (8) | -0.2660 (7) | 0.1496 (4) | 4.0 (5) |
| C19 | 0.3110 (8) | 0.0918 (7) | 0.1920 (4) | 4.1 (5) |
| C20 | -0.0352 (7) | -0.1463 (7) | 0.3099 (4) | 3.7 (5) |
| C21 | 0.1660 (8) | 0.0241 (8) | 0.0499 (4) | 4.9 (6) |
| C22 | 0.0977 (11) | 0.1002 (8) | 0.0064 (5) | 7.3 (9) |
| C23 | -0.0348 (9) | -0.1526 (8) | 0.0827 (5) | 5.5 (6) |
| C24 | -0.0472 (10) | -0.2121 (9) | 0.0190 (5) | 7.3 (9) |
| C25 | 0.5434 (7) | -0.1437 (8) | 0.2959 (5) | 5.1 (6) |
| C26 | 0.6277 (9) | -0.1362 (9) | 0.3523 (6) | 6.9 (8) |
| C27 | 0.2826 (8) | -0.3777 (8) | 0.4374 (5) | 4.8 (6) |
| C28 | 0.3124 (11) | -0.5191 (10) | 0.5232 (6) | 9.1 (9) |
| C29 | 0.3358 (8) | -0.4814 (8) | 0.4522 (5) | 5.3 (6) |
| C30 | 0.4548 (10) | -0.4834 (9) | 0.4351 (6) | 8.2 (8) |
| C31 | 0.5120 (11) | -0.3935 (14) | 0.4731 (8) | 12.5 (15) |
| O1 | 0.1468 (5) | 0.0444 (5) | 0.4035 (3) | 4.8 (4) |
| O2 | 0.2395 (6) | -0.0288 (6) | 0.0299 (3) | 6.2 (5) |
| O3 | 0.1278 (5) | 0.0259 (4) | 0.1150 (2) | 4.0 (3) |
| O4 | -0.1023 (7) | -0.0957 (6) | 0.1064 (4) | 7.8 (5) |
| O5 | 0.0621 (5) | -0.1729 (4) | 0.1125 (3) | 3.9 (3) |
| O6 | 0.2390 (6) | -0.3221 (6) | 0.4770 (3) | 6.4 (5) |
| O7 | 0.2919 (5) | -0.3565 (5) | 0.3700 (3) | 4.1 (3) |
| O8 | 0.5652 (6) | -0.1586 (8) | 0.2380 (4) | 9.2 (7) |
| O9 | 0.4431 (4) | -0.1283 (5) | 0.3207 (3) | 3.9 (3) |

Table 3. Bond lengths (Å) and angles (°)

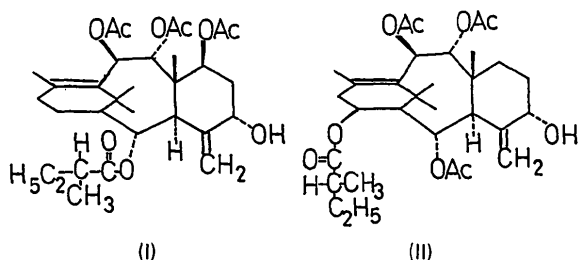
| | | | |
|---------|-----------|---------|-----------|
| C1—C2 | 1.54 (1) | C12—C20 | 1.51 (1) |
| C2—C3 | 1.55 (1) | C16—C17 | 1.56 (1) |
| C3—C8 | 1.59 (1) | C21—O2 | 1.19 (1) |
| C5—C6 | 1.50 (1) | C23—O4 | 1.19 (1) |
| C7—C8 | 1.56 (1) | C25—O8 | 1.18 (1) |
| C9—C10 | 1.54 (1) | C27—O6 | 1.18 (1) |
| C10—O5 | 1.456 (8) | C29—C30 | 1.47 (1) |
| C12—C13 | 1.52 (1) | C1—C16 | 1.55 (1) |
| C14—O7 | 1.455 (9) | C3—C4 | 1.52 (1) |
| C21—C22 | 1.54 (1) | C4—C15 | 1.35 (1) |
| C23—C24 | 1.47 (1) | C6—C7 | 1.55 (1) |
| C25—C26 | 1.50 (1) | C8—C19 | 1.52 (1) |
| C27—C29 | 1.52 (1) | C10—C11 | 1.49 (1) |
| C28—C29 | 1.50 (1) | C11—C16 | 1.54 (1) |
| C1—C14 | 1.51 (1) | C13—C14 | 1.54 (1) |
| C2—O9 | 1.467 (9) | C16—C18 | 1.53 (1) |
| C4—C5 | 1.49 (1) | C21—O3 | 1.354 (9) |
| C5—O1 | 1.40 (1) | C23—O5 | 1.33 (1) |
| C8—C9 | 1.55 (1) | C25—O9 | 1.32 (1) |
| C9—O3 | 1.474 (9) | C27—O7 | 1.35 (1) |
| C11—C12 | 1.35 (1) | C30—C31 | 1.54 (2) |

| | | | |
|-------------|-----------|-------------|-----------|
| C2—C1—C14 | 111.3 (6) | C2—C1—C16 | 114.2 (6) |
| C14—C1—C16 | 112.7 (6) | C1—C2—C3 | 117.0 (6) |
| C1—C2—O9 | 103.9 (6) | C3—C2—O9 | 108.7 (6) |
| C2—C3—C4 | 118.4 (6) | C2—C3—C8 | 116.4 (6) |
| C4—C3—C8 | 103.8 (6) | C3—C4—C5 | 112.9 (7) |
| C3—C4—C15 | 128.4 (7) | C5—C4—C15 | 118.0 (7) |
| C4—C5—C6 | 107.9 (6) | C4—C5—O1 | 113.0 (7) |
| C6—C5—O1 | 108.5 (7) | C5—C6—C7 | 113.6 (7) |
| C6—C7—C8 | 112.1 (7) | C3—C8—C7 | 106.1 (6) |
| C3—C8—C9 | 115.6 (6) | C3—C8—C19 | 111.0 (6) |
| C7—C8—C9 | 108.1 (6) | C7—C8—C19 | 111.1 (6) |
| C9—C8—C19 | 105.0 (6) | C8—C9—C10 | 119.4 (6) |
| C8—C9—O3 | 106.2 (6) | C10—C9—O3 | 102.0 (6) |
| C9—C10—C11 | 111.2 (6) | C9—C10—O5 | 106.6 (5) |
| C11—C10—O5 | 109.8 (6) | C10—C11—C12 | 119.0 (7) |
| C10—C11—C16 | 121.7 (6) | C12—C11—C16 | 118.2 (6) |
| C11—C12—C13 | 120.8 (7) | C11—C12—C20 | 126.1 (7) |
| C13—C12—C20 | 112.9 (6) | C12—C13—C14 | 113.0 (6) |
| C1—C14—C13 | 116.7 (6) | C1—C14—O7 | 105.9 (6) |
| C13—C14—O7 | 108.5 (6) | C1—C16—C11 | 105.0 (5) |
| C1—C16—C17 | 110.2 (6) | C1—C16—C18 | 111.4 (6) |
| C11—C16—C18 | 107.6 (6) | C11—C16—C18 | 118.6 (6) |
| C17—C16—C18 | 104.0 (6) | C22—C21—O2 | 126.0 (8) |
| C22—C21—O3 | 109.0 (8) | O2—C21—O3 | 125.0 (8) |
| C24—C23—O4 | 125.8 (9) | C24—C23—O5 | 110.8 (9) |
| O4—C23—O5 | 123.4 (8) | C26—C25—O8 | 124.5 (8) |
| C26—C25—O9 | 109.8 (8) | O8—C25—O9 | 125.7 (8) |
| C29—C27—O6 | 127.2 (8) | C29—C27—O7 | 109.3 (7) |
| O6—C27—O7 | 123.5 (8) | C27—C29—C28 | 112.7 (8) |
| C27—C29—C30 | 112.6 (8) | C28—C29—C30 | 112.8 (9) |
| C29—C30—C31 | 108.2 (9) | C9—O3—C21 | 117.3 (6) |
| C10—O5—C23 | 117.8 (6) | C14—O7—C27 | 116.7 (6) |
| C2—O9—C25 | 116.7 (6) | | |

Fig. 1. The molecular structure and labeling scheme of C₃₁H₄₆O₉ (taiwanxan).

all H atoms were fixed and not refined. Final $R(F) = 5.70\%$ ($wR = 6.18\%$), weighting scheme $w = 1/[\sigma^2(F) + (0.01F)^2]$, $\Delta/\sigma < 0.12$, peak in difference map $< 0.25 \text{ e } \text{\AA}^{-3}$. 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. Since the NMR spectrum of the isolated compound [taiwanxan, (II), m.p. = 500–503 K] indicates three acetyl groups (2.016, 2.028, 2.039) and an α -methylbutyrate group (0.88, *t*, *J* = 7.4 Hz; 1.11, *d*, *J* = 7 Hz), the structure is very similar to the known compound (I) (De Marciano & Halsall, 1969), tax-4(20),11-diene-2 α ,5 α ,7 β ,9 α ,10 β -pentol 7 β ,9 α ,10 β -triacetate 2 α - α -methylbutyrate, C₃₁H₄₆O₉, m.p. = 500–502 K. The structure of taiwanxan, (II), was revealed by X-ray single-crystal diffraction studies as tax-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.



Comparison of the NMR spectra of taiwanxan with that of compound (I) (see Table 1) confirmed that taiwanxan is a geometric isomer of compound (I).

An ORTEPB drawing is given in Fig. 1. The positional and isotropic thermal parameters are given in

Table 2.* Bond lengths and angles are given in Table 3. Compounds (I) and (II) have two differences: an α -methylbutyrate attaches to the 2 α position in compound (I) and 14 β in (II), while an acetate group attaches to 7 β in (I) and 2 α in (II). The geometry of the three acetyl groups in (II) is normal. Only C4–C15 and C11–C12 are double bonds. All the other C–C bonds in the skeleton are single.

The authors express their appreciation for support of this work to the National Science Council for a research grant and for the use of the CAD-4 diffractometer.

* Lists of anisotropic thermal parameters, structure factors and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43802 (23 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 of Methyl *trans*-Communate

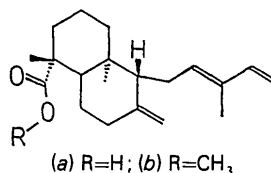
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Abstract. C₂₁H₃₂O₂, *M_r* = 316.47, orthorhombic, *P*2₁2₁2₁, *a* = 7.414 (2), *b* = 9.786 (3), *c* = 25.412 (4) Å, *V* = 1843.68 Å³, *Z* = 4, *D_x* = 1.14 g cm^{−3}, $\lambda(\text{Mo } K\alpha)$ = 0.7093 Å, $\mu(\text{Mo } K\alpha)$ = 0.72 cm^{−1}, *F*(000) = 696, *T* = 298 K, *R* = 0.051 for 1494 reflections. *trans*-Communic acid was isolated from the fresh leaves of *Calocedrus formosana* (florin) Florin, then converted into the crystalline methyl ester with diazomethane. The structure is confirmed by X-ray diffraction study.

Introduction. *trans*-Communic acid (*a*) has been isolated from the heartwood of *Juniperus communis* L. and converted with diazomethane into methyl *trans*-communate (*b*) (Arya, Erdtman & Kubota, 1961). *trans*-Communic acid has also been separated by chromatography from the bled resin of New Zealand kauri (Thomas, 1966).



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