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Structure of 12β-Benzoyloxy-3β,8β,14β,17β-tetrahydroxy-5-pregnene-20-one

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Abstract. 3β,8β,14β,17β-Tetrahydroxy-20-oxo-5-pregnen-12β-yl benzoate, $C_{28}H_{36}O_7$, M_r = 484·60, monoclinic, $P2_1$, a = 10·840 (3), b = 14·480 (3), c = 7·936 (2) Å, β = 100·33 (3)°, V = 1225·5 (5) Å^3, Z = 2, D_x = 1·301 g cm^{-3}, λ(Cu $K\alpha$) = 1·5418 Å, μ = 7·72 cm^{-1}, F(000) = 520, T = 295 K, R = 0·038 for 1716 reflections with $I > 3\sigma(I)$. Ring conformations are: A, C chair; B 8β,9α-half-chair; D 14β-envelope. The A/B, B/C and C/D ring junctions are quasi-*trans*, *trans* and *cis*, respectively. The configuration at C(17) is S.

Introduction. The title compound which was extracted from the roots of *Calotropis gigantea* is a potential contraceptive. It is a rare steroid in that it has a bulky substituent at C(12) and a 14β-hydroxyl group. The exact stereochemistry has been established by this X-ray analysis.

Experimental. Colorless plate crystals grown from an aqueous ethanol solution by slow evaporation at room temperature; crystal *ca* 0·6 × 0·5 × 0·1 mm, Rigaku AFC diffractometer, graphite-monochromated Cu $K\alpha$ radiation, $2\theta \le 120°$, ω–2θ scan, scan speed 2° min^{-1} in 2θ, ω-scan width (2·3 + 0·1tanθ)°, background measured for 10 s on either side of peak; cell parameters by least-squares fit to observed 2θ values for 20 centered reflections with $22 < 2\theta < 57°$; intensity checks for three standard reflections showed little (±1·4%) variation; 2062 independent reflections (h −12 to 12, k 0 to 16, l −8 to 0), 1716 (90·7%) observed with $I > 3\sigma(I)$ and used in refinement; Lp corrections, no absorption or extinction correction. Structure solved by direct methods and refined by full-matrix least squares on F with anisotropic thermal parameters using *SHELX*76 (Sheldrick, 1976); H atoms identified on a difference map and refined isotropically. $\sum w(|F_o| - |F_c|)^2$ minimized, with $w = k/[\sigma^2(F_o) + gF_o^2]$, $\sigma(F)$ from counting statistics, k and g optimized in the least-squares procedure (k = 1·00, g = 0·0049); wR = 0·038 for 1716 observed reflections, 459 variables, R = 0·040 for all data, S = 1·08, $(\Delta/\sigma)_{\max}$ = 1·188 [thermal parameter of H(O8)] in final refinement cycle; max. and min. heights in final difference map 0·17 and −0·22 e Å^{-3}, respectively. All calculations performed with *SHELX*76 on an IBM 3090. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final atomic parameters are in Table 1.† Atomic numbering scheme with the intraannular torsion angles and a stereoscopic view of the molecule are shown in Figs. 1 and 2, respectively. Bond lengths and angles are listed in Table 2.

Although most of the molecular dimensions are in agreement within 4σ with the average values of those of other Δ^5-derivatives (Duax, Weeks & Rohrer, 1976), those near the C/D ring junction show considerable differences. The C(13)—C(17) and C(13)—C(14) bonds are longer by 0·045 and 0·042 Å, respectively, and the C(12)—C(13)—C(17) and C(8)—C(14)—C(15) angles are smaller by 4·7 and 3·6°, respectively, than the average values.

Rings A and C assume a highly symmetrical chair conformation. Asymmetry parameters (Duax, Weeks & Rohrer, 1976) for ring A: C_s[C(3)] = 0·4° {ΔC_2[C(2)—C(3)] = 2·8°, ΔC_2[C(1)—C(2)] = 4·1°}; ring C: C_s[C(11)] = 2·2° {ΔC_2[C(9)—C(11)] = 4·3°, ΔC_2[C(8)—C(9)] = 7·2°}. Ring B has an 8β,9α-half-chair conformation. Mirror and twofold symmetries are equally dominant as indicated by ΔC_s[C(5)] = 10·5° {ΔC_2[C(5)—C(6)] = 12·8°}. Ring D has a 14β-envelope conformation with the pseudorotation parameters (Altona, Geise & Romers, 1968) Δ = 22·6° and φ_m = −42·2° {ΔC_s[C(13)] = 6·0°, ΔC_s[C(14)] = 25·3°, ΔC_2[C(13)—C(14)] = 13·2°}.

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† Lists of structure factors, anisotropic thermal parameters, coordinates of H atoms, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52246 (10 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Atomic coordinates* (× 10^4) *and thermal factors* ($Å^2 \times 10^3$)

	x	y	z	U_{eq}*
C(1)	3360 (3)	1772	9772 (5)	46
C(2)	3280 (3)	868 (3)	10796 (5)	54
C(3)	2169 (3)	910 (3)	11673 (4)	49
C(4)	980 (4)	1056 (3)	10377 (6)	64
C(5)	1076 (3)	1926 (3)	9373 (5)	50
C(6)	264 (3)	2585 (3)	9382 (5)	60
C(7)	295 (4)	3498 (3)	8507 (5)	60
C(8)	1050 (3)	3445 (2)	7052 (4)	41
C(9)	2305 (2)	2958 (2)	7696 (4)	33
C(10)	2178 (2)	1965 (2)	8426 (4)	36
C(11)	3106 (3)	2983 (2)	6283 (4)	37
C(12)	3347 (2)	3963 (2)	5755 (3)	36
C(13)	2140 (3)	4508 (2)	5033 (4)	40
C(14)	1271 (3)	4430 (3)	6425 (4)	44
C(15)	1900 (4)	5100 (3)	7828 (5)	55
C(16)	2532 (6)	5847 (3)	6944 (6)	76
C(17)	2392 (4)	5587 (3)	5041 (5)	55
C(18)	1533 (3)	4146 (3)	3260 (4)	51
C(19)	2049 (5)	1215 (3)	7012 (6)	65
C(20)	3542 (3)	5875 (2)	4288 (5)	64
C(21)	3368 (6)	6139 (6)	2468 (7)	108
C(22)	5319 (2)	3855 (2)	4834 (3)	39
C(23)	5961 (2)	3713 (2)	3356 (3)	38
C(24)	5295 (2)	3696 (2)	1694 (3)	45
C(25)	5925 (3)	3541 (2)	347 (3)	52
C(26)	7191 (3)	3413 (2)	648 (4)	50
C(27)	7858 (3)	3444 (2)	2293 (4)	50
C(28)	7250 (2)	3589 (2)	3659 (3)	45
O(3)	2004 (2)	65 (2)	12592 (4)	61
O(8)	349 (2)	2945 (2)	5640 (3)	58
O(12)	4076 (1)	3912 (1)	4378 (2)	40
O(14)	83 (2)	4821 (2)	5609 (4)	63
O(17)	1354 (3)	6056 (2)	4051 (5)	83
O(20)	4572 (2)	5879 (2)	5153 (4)	89
O(22)	5861 (2)	3890 (2)	6316 (2)	61

*$U_{eq} = \frac{1}{3}\sum_i\sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j$.

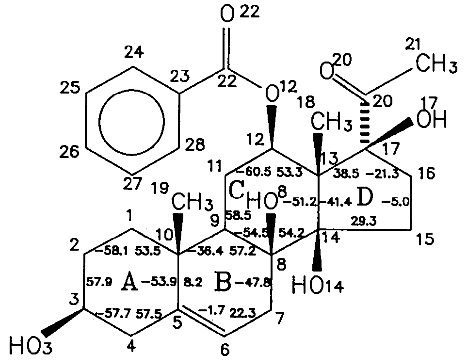

Fig. 1. Atomic numbering scheme and intraannular torsion angles.

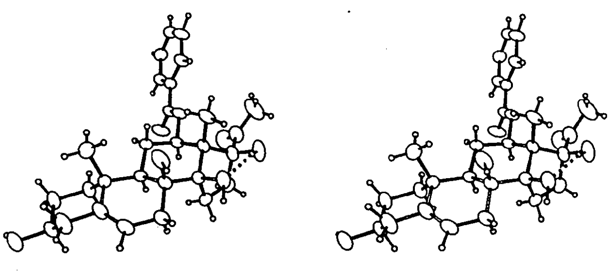

Fig. 2. A stereoscopic view of the molecule. The dotted line denotes the hydrogen bond.

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

C(1)—C(2)	1·551 (5)	C(1)—C(10)	1·539 (4)
C(2)—C(3)	1·496 (5)	C(3)—C(4)	1·513 (5)
C(3)—O(3)	1·453 (5)	C(4)—C(5)	1·503 (6)
C(5)—C(6)	1·299 (5)	C(5)—C(10)	1·522 (4)
C(6)—C(7)	1·496 (6)	C(7)—C(8)	1·533 (5)
C(8)—C(9)	1·535 (4)	C(8)—C(14)	1·544 (5)
C(8)—O(8)	1·433 (4)	C(9)—C(10)	1·567 (4)
C(9)—C(11)	1·537 (4)	C(10)—C(19)	1·550 (5)
C(11)—C(12)	1·516 (4)	C(12)—C(13)	1·547 (4)
C(12)—O(12)	1·461 (3)	C(13)—C(14)	1·579 (4)
C(13)—C(17)	1·586 (5)	C(13)—C(18)	1·535 (5)
C(14)—C(15)	1·540 (6)	C(14)—O(14)	1·448 (4)
C(15)—C(16)	1·518 (7)	C(16)—C(17)	1·537 (6)
C(17)—C(20)	1·533 (5)	C(17)—O(17)	1·424 (5)
C(20)—C(21)	1·473 (7)	C(20)—O(20)	1·201 (4)
C(22)—C(23)	1·482 (3)	C(22)—O(12)	1·334 (2)
C(22)—O(22)	1·218 (3)	C(23)—C(24)	1·385 (3)
C(23)—C(28)	1·386 (3)	C(24)—C(25)	1·387 (4)
C(25)—C(26)	1·362 (5)	C(26)—C(27)	1·375 (4)
C(27)—C(28)	1·382 (4)		

C(3)—C(2)—C(1)	109·5 (3)	C(4)—C(3)—C(2)	110·4 (3)
C(5)—C(4)—C(3)	110·2 (3)	C(5)—C(10)—C(1)	106·3 (3)
C(6)—C(5)—C(4)	120·1 (3)	C(7)—C(6)—C(5)	125·1 (3)
C(8)—C(7)—C(6)	111·4 (3)	C(9)—C(8)—C(7)	109·5 (3)
C(9)—C(10)—C(1)	107·8 (2)	C(9)—C(10)—C(5)	110·2 (2)
C(10)—C(1)—C(2)	113·5 (2)	C(10)—C(5)—C(4)	115·3 (3)
C(10)—C(5)—C(6)	124·6 (4)	C(10)—C(9)—C(8)	114·4 (2)
C(11)—C(9)—C(8)	109·2 (2)	C(11)—C(9)—C(10)	113·0 (2)
C(12)—C(11)—C(9)	111·8 (2)	C(13)—C(12)—C(11)	113·8 (2)
C(13)—C(14)—C(8)	116·0 (3)	C(14)—C(8)—C(7)	109·3 (3)
C(14)—C(8)—C(9)	110·6 (2)	C(14)—C(13)—C(12)	106·0 (2)
C(15)—C(14)—C(8)	115·0 (3)	C(15)—C(14)—C(13)	102·6 (3)
C(16)—C(15)—C(14)	107·0 (3)	C(16)—C(17)—C(13)	103·4 (3)
C(17)—C(13)—C(12)	111·6 (3)	C(17)—C(13)—C(14)	101·0 (3)
C(17)—C(16)—C(15)	107·9 (4)	C(18)—C(13)—C(12)	111·1 (3)
C(18)—C(13)—C(14)	113·9 (3)	C(18)—C(13)—C(17)	112·7 (3)
C(19)—C(10)—C(1)	109·4 (3)	C(19)—C(10)—C(5)	110·8 (3)
C(19)—C(10)—C(9)	112·2 (3)	C(20)—C(17)—C(13)	114·7 (3)
C(20)—C(17)—C(16)	111·9 (4)	C(21)—C(20)—C(17)	118·8 (4)
C(22)—O(12)—C(12)	117·2 (2)	C(24)—C(23)—C(22)	121·2 (2)
C(25)—C(24)—C(23)	119·4 (2)	C(26)—C(25)—C(24)	120·5 (2)
C(27)—C(26)—C(25)	120·2 (3)	C(27)—C(28)—C(23)	119·4 (2)
C(28)—C(23)—C(22)	118·8 (2)	C(28)—C(23)—C(24)	120·0 (2)
C(28)—C(27)—C(26)	120·4 (3)	O(3)—C(3)—C(2)	112·4 (3)
O(3)—C(3)—C(4)	107·0 (3)	O(8)—C(8)—C(7)	109·5 (3)
O(8)—C(8)—C(9)	110·1 (2)	O(8)—C(8)—C(14)	107·8 (3)
O(12)—C(12)—C(11)	107·6 (2)	O(12)—C(12)—C(13)	106·5 (2)
O(12)—C(22)—C(23)	112·9 (2)	O(14)—C(14)—C(8)	109·2 (3)
O(14)—C(14)—C(13)	104·7 (3)	O(14)—C(14)—C(15)	108·7 (3)
O(17)—C(17)—C(13)	110·4 (3)	O(17)—C(17)—C(16)	110·8 (4)
O(17)—C(17)—C(20)	105·8 (3)	O(20)—C(20)—C(17)	121·1 (3)
O(20)—C(20)—C(21)	120·1 (4)	O(22)—C(22)—C(23)	123·8 (2)
O(22)—C(22)—O(12)	123·2 (2)		

The ring junctions *A*/*B*, *B*/*C* and *C*/*D* are quasi-*trans*, *trans* and *cis*, respectively. The 14β-hydroxyl group which is a rare substituent in the steroids and the 18β-methyl group make the *C*/*D* ring junction *cis*. The β face is crowded and the steroid backbone exhibits a considerable bowing towards the α face. The C(19)—C(10)···C(13)—C(18) pseudotorsion angle, which represents the twist about the length of steroids, is 20·3°.

In most pregnanes studied crystallographically thus far, the 17-side chain containing a 20-keto substituent is β oriented. However, in the title compound, the 17-acetyl group is α oriented and the 17-hydroxyl group is β oriented so that the configuration at C(17) is *S*. From the numerous crystal structures, it has been observed that rotation of the 17-side chain is hindered despite apparent freedom of rotation and the C(16)—C(17)—C(20)—O(20) torsion angle is between 0 and −46° (Duax, Griffin & Rohrer, 1981). In the title compound the torsion angle is 32·1 (4)° which is in the normal range for an enantiomer.

The planar 12β-benzoyloxy group is approximately parallel to the 17α-acetyl plane, the dihedral angles with the C(5)—C(12)—C(14)—C(17) reference plane being 68 and 57°, respectively. The nearly perpendicular arrangement of the benzoyloxy moiety with respect to the steroidal nucleus seems to be the result of minimizing steric hindrances with the 17-acetyl group.

There is an intramolecular hydrogen bond [O(17)—H···O(14); H···O = 1·79 (7), O···O = 2·690 (4) Å, ∠OHO = 136 (5)°] but no intermolecular hydrogen bond. There is no C···C contact less than 3·5 Å and the shortest H···H distance is 2·23 Å.

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Struktur des Phosphasilacubans $(^t\mathrm{BuSiP})_4$†

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Abstract. 2,4,6,8-Tetra-*tert*-butyl-1,3,5,7-tetraphospha-2,4,6,8-tetrasilapentacyclo[4.2.0.0^{2,5}.0^{3,8}.0^{4,7}]octane, $C_{16}H_{36}P_4Si_4$, $M_r = 464{\cdot}699$, cubic, $P\bar{4}3n$, $a = 17{\cdot}409\ (4)$ Å, $V = 5276{\cdot}2$ Å^3, $Z = 8$, $D_x = 1{\cdot}1698$ Mg m^{-3}, $\lambda(\mathrm{Mo}\ K\alpha) = 0{\cdot}71069$ Å, $\mu = 0{\cdot}459$ mm^{-1}, $F(000) = 1984$, $T = 296$ K, $R_F = 0{\cdot}026$ for 578 reflections with $|F_o| \geq 4\sigma(F_o)$. Alternating P and ^{t}Bu-substituted Si atoms are arranged in a cubane-like molecule, which can be partitioned into a larger P_4 and a smaller Si_4 tetrahedron. The unit cell contains two independent $(^t\mathrm{BuSiP})_4$ molecules of symmetry $\bar{4}$ (S_4) and 23 (T), respectively, in the ratio 6:2. The main difference lies in the orientation of the ^{t}Bu substituents at the Si atoms. The bond lengths (Å) and angles (°) within the P—Si cage are d(P—Si) = 2·281 (2) (S_4), 2·278 (3) (T), φ(P—Si—P) = 101·61 (7) (S_4), 101·62 (9) (T), φ(Si—P—Si) = 77·03 (31) (S_4), 77·02 (9) (T). The geometric parameters of the substituents are normal.

Einleitung. Ein Silaphosphan mit Cuban-Struktur ist bisher nicht beschrieben worden, obwohl etliche Phosphor-Silicium-Heterocyclen bekannt sind (Fritz, 1987). Kürzlich gelang die Gewinnung des *closo*-Tetrakis(*tert*-butylsilaphosphan)s, $(^t\mathrm{BuSiP})_4$, durch die Umsetzung von $^t\mathrm{BuSiCl}_3$ mit $\mathrm{LiAl(PH_2)_4}$ (Baudler, Scholz, Tebbe & Fehér, 1989). Dieses erste Phosphasilacuban wurde hinsichtlich seiner Zusammensetzung durch Elementaranalyse und Molmassenbestimmung (MS) sowie bezüglich seiner Struktur durch schwingungsspektroskopische (IR, Raman) und NMR-spektroskopische Untersuchungen [^{31}P(^{1}H)-NMR, ^{1}H(^{31}P)-NMR, ^{29}Si(^{1}H)-DEPT-NMR] charakterisiert. Ziel der vorliegenden Arbeit ist die Bestimmung der metrischen Parameter des Moleküls und Kristalls dieser neuartigen Verbindung.

Experimentelles. Farblose Platten, Würfel und Tetraeder, F.P. ≈ 597 K, quaderförmiger Kristall (0,38 × 0,38 × 0,25 mm), in einer Glaskapillare festgeklemmt und unter Argon eingeschmolzen. CAD-4 Enraf–Nonius Diffraktometer, Mo $K\alpha$-Strahlung, Graphit-Monochromator, 50 kV, 32 mA, Scintillationszähler, ω–θ-Scan, Abtastbreite $\Delta\omega = \pm(1{,}0 + 0{,}35\ \mathrm{tg}\theta)°$, Apertur $4{,}0 \times (1{,}3 + 1{,}0\ \mathrm{tg}\theta)$ mm^2, variable Abtastgeschwindigkeit $3{,}30 \leq v \leq 5{,}49°$ min^{-1}, $(\sin\theta)/\lambda \leq 0{,}639$ Å^{-1}, $0 \leq h,k,l \leq 22$, 6348 Reflexe, Meßzeit 92,5 h, Kontrolle der zeitlichen Intensitätsänderung ($1{,}000 \leq K \leq 1{,}028$) und der Absorptionseffekte (ψ-Scans für neun Reflexe, $0{,}988 \leq A^* \leq 1{,}000$),

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