

Structure of Ptaquiloside Tetraacetate,  $C_{28}H_{38}O_{12}$ 

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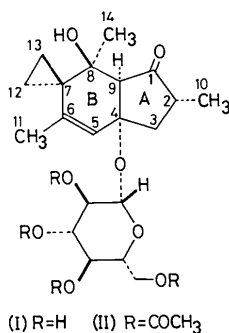
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**Abstract.**  $M_r = 566.6$ , orthorhombic,  $P2_12_12_1$ ,  $a = 15.900$  (2),  $b = 18.158$  (3),  $c = 10.252$  (2) Å,  $V = 2960.0$  (8) Å<sup>3</sup>,  $Z = 4$ ,  $D_x = 1.27$  Mg m<sup>-3</sup>, Mo  $K\alpha_1$ ,  $\lambda = 0.70926$  Å,  $\mu = 0.093$  mm<sup>-1</sup>,  $F(000) = 1208$ ,  $T = 299$  (2) K, final  $R = 0.044$  for 2520 observed unique reflections. Ptaquiloside is shown to be a novel norsesquiterpene with the *cis*-fused illudane skeleton and the allylic tertiary hydroxyl group forming a  $\beta$ -glycosidic linkage with D-(+)-glucose.

**Introduction.** Ptaquiloside (I), a carcinogenic substance isolated from the bracken *Pteridium aquilinum* var. *latiusculum*, is a new norsesquiterpene glucoside (Niwa, Ojika, Wakamatsu, Yamada, Hirono & Matsushita, 1983; Hirono, Yamada, Niwa, Shizuri, Ojika, Hosaka, Yamaji, Wakamatsu, Kigoshi, Niiyama & Uosaki, 1984). Crystallization of (I) failed; therefore the crystal-structure analysis of ptaquiloside tetraacetate (II) has been undertaken to determine the structure.



**Experimental.** Crystal specimens obtained from methanol solutions.  $D_m$  not determined. Crystal  $0.55 \times 0.55 \times 0.60$  mm. Rigaku AFC-5 four-circle diffractometer, graphite-monochromatized Mo  $K\alpha$ , Laue group *mmm*. Cell parameters refined by least-squares

methods on the basis of 20  $2\theta$  values ( $36 < 2\theta < 39^\circ$ ). Intensity measurement performed to  $2\theta = 55^\circ$ ,  $\theta$ - $2\theta$  scan technique, scan speed  $2^\circ \text{ min}^{-1}(\theta)$ . Five standard reflections showed no significant variation,  $0.987 < |F_o|/|F_o|_{\text{initial}} < 1.022$ . Space group  $P2_12_12_1$  determined from systematic absences ( $h00$ ,  $h$  odd;  $0k0$ ,  $k$  odd;  $00l$ ,  $l$  odd). 3835 reflections measured, 472 weak reflections classified as unobserved [ $|F_o| \leq 3\sigma(|F_o|)$ ], 843 zero and 2520 observed unique reflections. Lorentz-polarization correction, no absorption correction. Structure solved by direct methods with MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). 35 among 40 non-H atoms determined from  $E$  map and the others from Fourier synthesis; block-diagonal least-squares refinement with anisotropic thermal parameters using UNICSIII computation program system (Sakurai & Kobayashi, 1979). All H atoms found from difference synthesis and refined with isotropic thermal parameters.  $\sum w||F_o| - |F_c||^2$  minimized,  $w^{-1} = \sigma^2(|F_o|) + (0.015|F_o|)^2$ . Final  $R = 0.044$ ,  $wR = 0.048$ ,  $S = 2.0$ .  $\Delta/\sigma < 0.4$  for non-H atoms and  $< 1.4$  for H atoms. Max. and min. height in final difference synthesis  $\pm 0.2 e \text{ \AA}^{-3}$ . Complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974).

Under alkaline conditions both ptaquiloside (I) and ptaquiloside tetraacetate (II) released D-(+)-glucose, which was identified by the <sup>1</sup>H and <sup>13</sup>C NMR spectra and the specific rotation. Based on the absolute

\* Lists of structure factors, anisotropic thermal parameters, atomic parameters for H atoms, bond lengths involving H atoms and those in the tetraacetylglucoside moiety, torsion angles, and deviations of atoms from the least-squares planes have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39576 (32 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

configuration of D-(+)-glucose, which has already been established (Neidle & Rogers, 1970), the absolute structure of ptaquiloside tetraacetate (II) was determined.

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters (Hamilton, 1959)

	x	y	z	$B_{eq}(\text{\AA}^2)$
O(1)	6404 (2)	2074 (2)	4451 (3)	5.7
O(2)	3997 (1)	2222 (1)	7040 (2)	2.9
O(3)	5501 (2)	742 (1)	4570 (3)	5.4
O(4)	2601 (1)	1413 (1)	7823 (2)	3.3
O(5)	1594 (1)	2060 (1)	9821 (2)	3.6
O(6)	1516 (1)	3650 (1)	9686 (2)	3.5
O(7)	3511 (1)	3239 (1)	8110 (2)	3.0
O(8)	3510 (1)	4213 (1)	10322 (2)	3.9
O(9)	3209 (3)	760 (2)	9404 (4)	9.6
O(10)	635 (2)	1688 (2)	8384 (3)	7.2
O(11)	1620 (2)	3520 (2)	11832 (2)	6.8
O(12)	2774 (2)	5099 (2)	11299 (3)	6.5
C(1)	5761 (2)	2337 (2)	4893 (3)	3.9
C(2)	5535 (2)	3142 (2)	4896 (3)	4.4
C(3)	4835 (2)	3184 (2)	5928 (4)	4.2
C(4)	4365 (2)	2446 (2)	5794 (3)	3.1
C(5)	3753 (2)	2468 (2)	4707 (3)	3.6
C(6)	3787 (2)	2063 (2)	3629 (3)	3.7
C(7)	4422 (2)	1476 (2)	3468 (3)	3.7
C(8)	4793 (2)	1209 (2)	4760 (3)	3.6
C(9)	5067 (2)	1892 (2)	5536 (3)	3.0
C(10)	6276 (3)	3662 (3)	5095 (5)	8.2
C(11)	3176 (3)	2192 (3)	2520 (4)	6.3
C(12)	4342 (3)	910 (2)	2387 (4)	5.5
C(13)	4985 (3)	1509 (3)	2280 (4)	5.4
C(14)	4151 (2)	759 (2)	5501 (4)	4.1
C(15)	3277 (2)	2581 (2)	7450 (3)	2.7
C(16)	2824 (2)	2091 (2)	8429 (3)	2.6
C(17)	2029 (2)	2486 (2)	8856 (3)	2.8
C(18)	2266 (2)	3222 (2)	9451 (3)	2.8
C(19)	2796 (2)	3665 (2)	8500 (3)	3.0
C(20)	3117 (2)	4371 (2)	9095 (4)	4.0
C(21)	2816 (2)	781 (2)	8423 (4)	4.7
C(22)	2505 (3)	138 (2)	7699 (5)	6.1
C(23)	893 (2)	1692 (2)	9465 (4)	3.9
C(24)	488 (3)	1314 (2)	10572 (4)	5.5
C(25)	1269 (2)	3757 (2)	10928 (3)	4.1
C(26)	515 (3)	4253 (3)	10958 (4)	7.1
C(27)	3288 (2)	4621 (2)	11352 (4)	4.3
C(28)	3749 (3)	4396 (3)	12540 (4)	6.1

Table 2. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ )

O(1)—C(1)	1.216 (5)	C(4)—C(9)	1.526 (5)
O(2)—C(4)	1.463 (4)	C(5)—C(6)	1.329 (5)
O(2)—C(15)	1.383 (4)	C(6)—C(7)	1.477 (5)
O(3)—C(8)	1.423 (4)	C(6)—C(11)	1.514 (5)
C(1)—C(2)	1.505 (5)	C(7)—C(8)	1.529 (4)
C(1)—C(9)	1.518 (5)	C(7)—C(12)	1.517 (5)
C(2)—C(3)	1.538 (5)	C(7)—C(13)	1.513 (5)
C(2)—C(10)	1.524 (6)	C(8)—C(9)	1.536 (5)
C(3)—C(4)	1.540 (5)	C(8)—C(14)	1.512 (5)
C(4)—C(5)	1.480 (4)	C(12)—C(13)	1.497 (7)
C(4)—O(2)—C(15)	117.7 (2)	C(6)—C(7)—C(8)	113.3 (3)
O(1)—C(1)—C(2)	125.7 (3)	C(6)—C(7)—C(12)	120.9 (3)
O(1)—C(1)—C(9)	124.3 (3)	C(6)—C(7)—C(13)	117.8 (3)
C(2)—C(1)—C(9)	110.0 (3)	C(8)—C(7)—C(12)	116.8 (3)
C(1)—C(2)—C(3)	102.8 (3)	C(8)—C(7)—C(13)	118.8 (3)
C(1)—C(2)—C(10)	114.7 (3)	C(12)—C(7)—C(13)	59.2 (3)
C(3)—C(2)—C(10)	115.9 (3)	O(3)—C(8)—C(7)	112.1 (3)
C(2)—C(3)—C(4)	104.3 (3)	O(3)—C(8)—C(9)	109.1 (3)
O(2)—C(4)—C(3)	111.0 (3)	O(3)—C(8)—C(14)	106.3 (3)
O(2)—C(4)—C(5)	113.7 (3)	C(7)—C(8)—C(9)	107.6 (3)
O(2)—C(4)—C(9)	105.1 (3)	C(7)—C(8)—C(14)	110.3 (3)
C(3)—C(4)—C(5)	111.3 (3)	C(9)—C(8)—C(14)	111.6 (3)
C(3)—C(4)—C(9)	103.5 (3)	C(1)—C(9)—C(4)	104.8 (3)
C(5)—C(4)—C(9)	111.6 (3)	C(1)—C(9)—C(8)	114.3 (3)
C(4)—C(5)—C(6)	125.8 (3)	C(4)—C(9)—C(8)	114.5 (3)
C(5)—C(6)—C(7)	121.3 (3)	C(7)—C(12)—C(13)	60.3 (3)
C(5)—C(6)—C(11)	120.9 (3)	C(7)—C(13)—C(12)	60.5 (3)
C(7)—C(6)—C(11)	117.8 (3)		

**Discussion.** Final atomic coordinates and selected bond lengths and bond angles are presented in Tables 1 and 2, respectively. A perspective view of the molecule is shown in Fig. 1. Table 1 and Fig. 1 represent the configuration of the molecule based on the absolute configuration of D-(+)-glucose. The molecular structure established by spectral and chemical means was confirmed. The norsesquiterpene has the same arrangement of rings as the antitumor factor illudin-S (lampterol) isolated from the Japanese mushroom *Lampteromyces japonicus* (Kawam.) Sing (Nakanishi, Ohashi, Tada & Yamada, 1965). A spiro cyclopropane moiety is attached to the six-membered ring *B*. Bond angles C(12)—C(7)—C(13) and C(6)—C(7)—C(8) are  $59.2(3)$  and  $113.3(3)^\circ$ , respectively. The mean value of the other C—C(7)—C angles is  $118.6(3)^\circ$ . The ring junction between ring *B* and the five-membered ring *A* is *cis*. Torsion angles C(3)—C(4)—C(9)—C(1) and C(5)—C(4)—C(9)—C(8) are  $-27.2(3)$  and  $-33.2(4)^\circ$ , respectively. Ring *A* adopts an envelope conformation, *i.e.* C(3) deviates by  $0.569(6)$  Å from the least-squares plane *A* of C(1), C(2), C(4) and C(9). In the *B* ring C(4), C(5), C(6) and C(9) are nearly planar with a maximum deviation of  $0.001$  Å and C(7) and C(8) deviate from plane *B* by  $0.144(7)$  and  $0.764(7)$  Å on the same side. Planes *A* and *B* make an angle of  $96.1(2)^\circ$ . The glycosidic linkage of D-(+)-glucose has the  $\beta$  configuration. There is an intramolecular hydrogen bond between O(3) and O(1), where the O(3)...O(1), O(3)—H(O3) and H(O3)...O(1) distances are  $2.815(4)$ ,  $0.77(4)$  and  $2.19(4)$  Å, respectively.

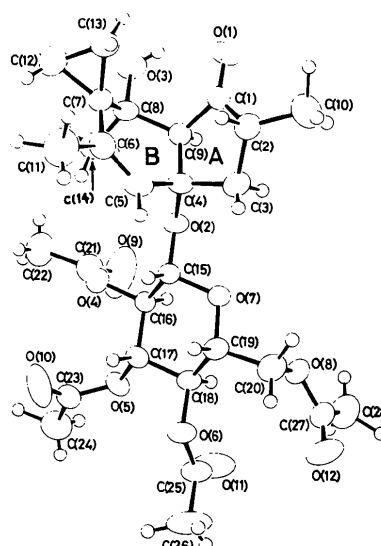


Fig. 1. An ORTEP drawing (Johnson, 1965) of the molecule with thermal ellipsoids scaled at the 50% probability level. H atoms are represented by circles of radius 0.08 Å.

The crystal structure consists of discrete molecules separated by normal van der Waals distances, except for a short intermolecular distance of 2.957 (5) Å for  $O(3) \cdots C(27)(1-x, -\frac{1}{2}+y, \frac{3}{2}-z)$ .

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## 1,2,5,6,7,8,9,10-Octa-*tert*-butyl-1,2,5,6,7,8,9,10-octaphospha-3,4-disila-dispiro[2.0.4.2]decan, \* $C_{32}H_{72}P_8Si_2$

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(Eingegangen am 27. Dezember 1983; angenommen am 15. Juni 1984)

**Abstract.**  $M_r = 760.89$ , monoclinic,  $C2/c$ ,  $a = 35.296$  (10),  $b = 14.442$  (3),  $c = 18.501$  (6) Å,  $\beta = 105.37$  (2)°,  $V = 9093.49$  Å<sup>3</sup>,  $Z = 8$ ,  $D_m = 1.11$ ,  $D_x = 1.111$  Mg m<sup>-3</sup>,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu(\text{Mo } K\alpha) = 0.372$  mm<sup>-1</sup>,  $F(000) = 3296$ ,  $T = 293$  K,  $R_F = 0.047$  for 3817 observed reflections [ $|F| \geq 4\sigma(F)$ ].  $(t\text{-BuP})_8\text{Si}_2$  forms a dispiro compound with a  $P_4\text{Si}$ , a  $P_2\text{Si}_2$  and a  $P_2\text{Si}$  ring connected nearly orthogonally by means of the Si atoms as spiro centres. The different surroundings of Si lead to endocyclic bond angles  $\varphi(\text{P-Si-P})$  between 59.1 and 107.5° ( $\sigma \leq 0.1^\circ$ ). These different bond-angle distortions at Si yield a significant variation of bond lengths  $d(\text{Si-P})$  from 2.233 to 2.317 Å ( $\sigma \approx 0.002$  Å).

**Einleitung.** Durch Cyclokondensation von  $K_2(t\text{-BuP})_2$  mit  $\text{SiCl}_4$  konnte das Spirane  $(t\text{-BuP})_2\text{Si}(t\text{-BuP})_2$  als Gemisch aus zwei Konfigurationsisomeren der Symmetrie  $\bar{4}$  und 2 dargestellt werden. Diese wurden nach

\* Beiträge zur Strukturchemie phosphorhaltiger Ketten und Ringe. 12. Teil 11: Tebbe & Heinlein (1984); Ergebnisse dieser Untersuchung sind bereits am 9. August 1983 in Lüttich während des ECM8 vorgestellt (Fehér, Heinlein & Tebbe, 1983) und zusammen mit den präparativen und spektroskopischen Ergebnissen kurz mitgeteilt worden (Baudler, Pontzen, Schings, Tebbe & Fehér, 1983).

fraktionierter Kristallisation aus *n*-Pentan getrennt isoliert (Baudler & Pontzen, 1982). Inzwischen liegen Röntgenstrukturanalysen der beiden Diastereomeren vor (Tebbe & Heinlein, 1984). Thermolyseversuche ergaben nun, dass das Isomer der Symmetrie  $\bar{4}$  oder auch das Isomergemisch in der Schmelze zu einem Dispiran  $(t\text{-BuP})_8\text{Si}_2$  dimerisiert (Baudler *et al.*, 1983). Diese neue Verbindung ist bei 'all-*trans*'-Stellung der *tert*-Butylsubstituenten aus einem  $P_2\text{Si}_2$ -Vierring aufgebaut, der über die beiden Siliciumatome mit einem  $P_2\text{Si}$ -Dreiring und mit einem  $P_4\text{Si}$ -Fünfring spiro-cyclisch verknüpft ist. Ziele der hier beschriebenen Röntgenstrukturanalyse sind die Bestätigung der Konstitution dieses ersten Spiro-Ringsystems aus einem Drei-, Vier- und Fünfring, die Absicherung der Konfiguration, die Ermittlung der Konformation im Kristall und die Vermessung des gesamten Moleküls. Darüber hinaus sollen ergänzende Strukturdaten für eine vergleichende Diskussion der Bindungsverhältnisse in Phosphor-Silicium-Verbindungen gewonnen werden. Bisher liegen Röntgenstrukturanalysen für so unterschiedliche Verbindungen wie die beiden Konfigurationsisomeren Spirane  $(t\text{-BuP})_2\text{Si}(t\text{-BuP})_2$  (Tebbe & Heinlein, 1984), den Dreiring  $(t\text{-BuP})_2\text{SiPh}_2$  (Tebbe, 1980), die Sechsringe  $[\text{Me}_2\text{Si}(t\text{-BuP})_2]_2$  (Fröhlich & Tebbe, 1982),  $[\text{PhP}(\text{SiMe}_2)_2]_2$  (Cordes, Schubert &