

hydrogène N(1)⋯HN(2) dont les caractéristiques sont les suivantes: (I) N(2)⋯N(1ⁱ)[(i) 1 + x, y, z] 2,971 (6), N(2)—H(20) 1,17 (4), N(1ⁱ)⋯H(20) 1,83 (5) Å, N(1ⁱ)⋯H(20)—N(2) 164 (1)^o; (II) N(2)⋯N(1ⁱ)[(i) $\frac{1}{2} + x$, $\frac{1}{2} - y$, $\frac{1}{2} + z$] 3,015 (6), N(2)—H(20) 1,08 (5), N(1ⁱ)⋯H(20) 2,17 (5) Å, N(1ⁱ)⋯H(20)—N(2) 132 (1)^o.

Il faut souligner ici une omission dans l'article de Sbit *et al.* (1988): dans (III), il y a également une liaison hydrogène N(1)⋯HN(2) caractérisée par N(2)⋯N(1ⁱ)[(i) x, 1 + y, z] 2,971 (3), N(2)—H 0,98 (2), N(1ⁱ)⋯H 2,06 (2) Å et N(1ⁱ)⋯H—N(2) 154 (1) Å.

Les auteurs remercient M. M. Vermeire pour les mesures diffractométriques et le Fonds National de la Recherche Scientifique pour le crédit allowé.

Références

- BASS, A. S. & ROBIE, N. W. (1984). *J. Pharmacol. Exp. Ther.* **229**, 67–71.
 BOUDET-DALBIN, R., DURAND, S., ADAM, Y., MOREAU, R. C. & FOUSSART-BLANPIN, O. (1986). *Eur. J. Med. Chem. Chim. Ther.* **21**, 131–137.

- BOUDET-DALBIN, R., GRASSY, G., ADAM, Y. & MOREAU, R. C. (1986). *Eur. J. Med. Chem. Chim. Ther.* **21**, 205–212.
 CESARIO, M., PASCARD, C., EL MOUKHTARI, M. & JUNG, L. (1981). *Eur. J. Med. Chem. Chim. Ther.* **16**, 13–17.
 COLLIN, S., NORBERG, B., EVRARD, G., DURANT, F., TOLLENAERE, J. P. & MOERBEELS, H. (1988). *Eur. J. Med. Chem. Chim. Ther.* **23**, 69–76.
 COLLIN, S., VERCAUTEREN, D. P., EVRARD, G. & DURANT, F. (1989). *J. Chem. Soc. Perkin Trans. 2*, pp. 407–412.
 DE PAULIS, T., KUMAR, Y., JOHANSSON, L., RÅMSBY, S., HALL, H., SÄLLEMARK, M., ÅNGEBY-MÖLLER, K. & ÖGREN, S. O. (1986). *J. Med. Chem.* **29**, 61–69.
 FURAYA, T., IWANAMI, S., TAKENATA, A. & SASADA, Y. (1982). *Bull. Chem. Soc. Jpn.* **55**, 2321–2326.
 NORTH, A. C. T., PHILLIPS, D. C. & MATHEWS, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
 NYBURG, S. C. & FAERMAN, C. H. (1985). *Acta Cryst.* **B41**, 274–279.
 SBIT, M., DUPONT, L., DIDEBERG, O., LIÉGEOIS, J. F. & DELARGE, J. (1988). *Acta Cryst.* **C44**, 907–909.
 SHELDRICK, G. M. (1976). *SHELX76*. Programme pour la détermination des structures cristallines. Univ. de Cambridge, Angleterre.
 SHELDRICK, G. M. (1986). *SHELXS86*. Programme pour la solution des structures cristallines. Univ. de Göttingen, République Fédérale d'Allemagne.
 VAN DE WATERBEEMD, H. & TESTA, B. (1981). *Helv. Chim. Acta*, **64**, 2183–2188.
 VAN DE WATERBEEMD, H. & TESTA, B. (1983). *J. Med. Chem.* **26**, 203–207.

Acta Cryst. (1990). **C46**, 1866–1869

Structure of Naringin Hexahemihydrate

BY GUANG-ZHU JIN, SATOSHI FUJII AND KEN-ICHI TOMITA

Faculty of Pharmaceutical Sciences, Osaka University, 1-6 Yamadaoka, Suita, Osaka 565, Japan

(Received 17 November 1989; accepted 11 December 1989)

Abstract. 7-[[2-O-(6-Deoxy- α -L-mannopyranosyl)- β -D-glucopyranosyl]oxy]-2,3-dihydro-5-hydroxy-2-(4-hydroxyphenyl)-4H-1-benzopyran-4-one hexahemihydrate, C₂₇H₃₂O₁₄·6·5H₂O, *M*_r = 697·66, monoclinic, *C*2, *a* = 22·394 (8), *b* = 7·350 (1), *c* = 20·354 (7) Å, β = 94·84 (4)^o, *V* = 3337 (2) Å³, *Z* = 4, *D*_m = 1·389 (2), *D*_x = 1·389 Mg m⁻³, λ (Cu *K* α) = 1·54178 Å, μ = 0·996 mm⁻¹, *F*(000) = 1484, *T* = 283 K, final *R* = 0·064 for 2725 observed reflections. The skeleton of the 4-hydroxyphenylbenzopyranone group is nearly planar, the dihedral angle between the hydroxyphenyl plane and the benzene ring of the benzopyranone being 11·3 (3)^o. The pyranone ring adopts a flattened 1,2-diplanar conformation. In the benzopyranone ring, an intramolecular hydrogen bond is formed between the carbonyl group and the hydroxyl group. A widely spread stacking interaction is found between two roughly planar 4-hydroxyphenylbenzopyranone groups which are related by

a twofold screw symmetry with about 3·68 Å separation.

Introduction. As one of the natural flavonoids, naringin is widely distributed among plants. This compound can be used for the maintenance of normal blood-vessel conditions by decreasing capillary permeability and fragility. Furthermore, it exhibits some biological activities, such as inhibitory action for aldose reductase (Varma & Kinoshita, 1976). In order to clarify its conformation and structure–function relationships, we carried out an X-ray structure determination and the structure is compared with those of the related compounds having a similar flavanone skeleton.

Experimental. Naringin purchased from Ishizu Seiyaku Co. Ltd, crystallized from aqueous methanol solution, density by flotation in xylene–chloroform

mixture; crystal dimensions $0.6 \times 0.16 \times 0.03$ mm; Rigaku automatic four-circle diffractometer (AFC-5R-300); ω - 2θ scanning technique ($2\theta_{\max} = 126^\circ$); graphite-monochromatized Cu $K\alpha$ radiation; unit-cell dimensions by least-squares procedure based on 2θ values ($29 < 2\theta < 56^\circ$) of 44 reflections; intensity fluctuation ($< 2.1\%$) monitored periodically by three reflections ($\bar{4}25$, $5\bar{3}1$, $5\bar{1}5$); 2949 unique reflections ($-26 \leq h \leq 26$, $-8 \leq k \leq 0$, $-24 \leq l \leq 0$), $R_{\text{int}} = 0.035$; Lorentz and polarization corrections, but not for absorption. Structure solved by *SHELXS86* (Sheldrick, 1986); structure first refined by full-matrix least squares with isotropic temperature factors, and then by block-diagonal least squares with anisotropic temperature factors for all non-H atoms; all H atoms located from a difference Fourier map; the final refinement including H atoms with constant isotropic temperature factors reduced R to 0.064 ($wR = 0.062$, $S = 3.36$) for 2725 observed reflections ($F_o \neq 0$) and 614 variables; function minimized $\sum w(|F_o| - k|F_c|)^2$, where $w = 1/\sigma^2(F_o)$ and k is the scale factor; highest and lowest residuals in final difference Fourier map 0.34 and $-0.24 e \text{ \AA}^{-3}$; $(\Delta/\sigma)_{\max} = 0.26$ for non-H atoms; scattering factors from *International Tables for X-ray Crystallography* (1974); program system *UNICS* (1979) on the ACOS 930 computer of the Protein Engineering Research Center, Institute for Protein Research, Osaka University.

Discussion. Final positional and thermal parameters of non-H atoms are listed in Table 1.* Bond distances and angles are given in Table 2. The molecular conformation with atomic numbering is given in Fig. 1. The large temperature factors for C(3), C(4), O(4) and O(5) atoms in the vertical direction of the benzopyranone ring plane are due to large thermal vibration (libration) of the ring.

The skeleton of the 4-hydroxyphenylbenzopyranone group is nearly planar. The benzene ring in the benzopyranone group and the phenyl rings are both essentially planar; the largest deviation from the individual least-squares plane is -0.015 (8) Å for the C(5) atom in the benzene ring and 0.007 (8) Å for the C(11) atom in the phenyl ring. The benzene ring is nearly parallel to the phenyl ring with a dihedral angle of 11.3 (3)°, while in many reported flavanone derivatives the dihedral angles are usually large, that is, the phenyl ring is nearly perpendicular to the benzene ring with angles of 85.5° in 5,7,14-trihydroxyflavanone, naringenin (Shin & Lah, 1986),

Table 1. Atomic coordinates and thermal parameters of non-H atoms

$$B_{\text{eq}} = (4/3)\sum_i \beta_i \mathbf{a}_i \cdot \mathbf{a}_i$$

	x	y	z	B_{eq} (Å ²)
O(1)	0.7375 (1)	0.5437 (7)	0.4568 (2)	4.3 (1)
C(2)	0.7289 (3)	0.5745 (14)	0.5228 (3)	6.3 (3)
C(3)	0.6762 (3)	0.5482 (31)	0.5469 (3)	16.2 (7)
C(4)	0.6216 (3)	0.5652 (23)	0.5010 (3)	11.3 (5)
O(4)	0.5712 (2)	0.5759 (22)	0.5205 (2)	20.0 (6)
C(5)	0.5823 (2)	0.5497 (13)	0.3828 (3)	6.0 (2)
O(5)	0.5249 (2)	0.5575 (13)	0.3993 (2)	10.0 (3)
C(6)	0.5920 (2)	0.5401 (11)	0.3172 (2)	4.4 (2)
C(7)	0.6505 (2)	0.5320 (8)	0.3001 (2)	3.0 (1)
O(7)	0.6559 (1)	0.5193 (6)	0.2343 (1)	3.3 (1)
C(8)	0.6994 (2)	0.5352 (9)	0.3474 (2)	3.4 (1)
C(9)	0.6885 (2)	0.5449 (9)	0.4126 (2)	3.6 (1)
C(10)	0.6304 (2)	0.5564 (13)	0.4326 (3)	5.5 (2)
C(11)	0.7886 (2)	0.5576 (10)	0.5633 (3)	4.5 (2)
C(12)	0.8419 (3)	0.5696 (14)	0.5341 (3)	6.6 (3)
C(13)	0.8965 (3)	0.5568 (15)	0.5708 (3)	7.4 (3)
C(14)	0.8969 (3)	0.5316 (13)	0.6376 (3)	5.9 (2)
O(14)	0.9537 (2)	0.5134 (11)	0.6737 (2)	7.7 (2)
C(15)	0.8455 (3)	0.5170 (11)	0.6682 (3)	4.7 (2)
C(16)	0.7908 (3)	0.5290 (11)	0.6309 (3)	4.7 (2)
C(1')	0.7139 (2)	0.5012 (8)	0.2131 (2)	3.1 (1)
C(2')	0.7083 (2)	0.4408 (7)	0.1422 (2)	2.7 (1)
O(2')	0.6842 (1)	0.2581 (5)	0.1378 (1)	3.1 (1)
C(3')	0.7703 (2)	0.4370 (7)	0.1167 (2)	2.7 (1)
O(3')	0.7667 (1)	0.3919 (5)	0.0496 (1)	3.2 (1)
C(4')	0.8014 (2)	0.6225 (8)	0.1282 (2)	3.0 (1)
O(4')	0.8623 (1)	0.6101 (6)	0.1123 (2)	3.6 (1)
C(5')	0.8000 (2)	0.6781 (8)	0.1999 (2)	3.1 (1)
C(6')	0.8240 (3)	0.8683 (9)	0.2120 (3)	4.2 (2)
C(6'')	0.7398 (1)	0.6771 (5)	0.2174 (2)	3.2 (1)
O(7')	0.8319 (2)	0.9121 (6)	0.2809 (2)	5.2 (1)
C(1'')	0.6383 (2)	0.2329 (8)	0.0868 (2)	3.0 (1)
C(2'')	0.6362 (2)	0.0322 (9)	0.0693 (2)	3.3 (1)
O(2'')	0.5970 (2)	0.0144 (6)	0.0103 (2)	4.0 (1)
C(3'')	0.6113 (2)	-0.0737 (8)	0.1251 (2)	3.5 (1)
O(3'')	0.6031 (2)	-0.2598 (6)	0.1030 (2)	4.3 (1)
C(4'')	0.5538 (2)	0.0028 (8)	0.1441 (2)	3.2 (1)
O(4'')	0.5374 (2)	-0.0939 (6)	0.2012 (2)	4.2 (1)
C(5'')	0.5604 (2)	0.2059 (9)	0.1607 (2)	3.3 (1)
C(6'')	0.5020 (2)	0.2970 (10)	0.1736 (3)	4.5 (2)
O(6'')	0.5826 (1)	0.2981 (5)	0.1055 (2)	3.1 (1)
O(W1)	0.5634 (3)	0.8937 (11)	0.6191 (3)	10.9 (3)
O(W2)	0.4282 (4)	0.2697 (10)	0.3577 (4)	12.6 (3)
O(W3)	0.8040 (2)	0.0538 (6)	0.0482 (2)	4.9 (1)
O(W4)	0.9232 (2)	0.3185 (7)	0.1738 (2)	5.0 (1)
O(W5)	0.8560 (2)	1.2778 (7)	0.2779 (2)	6.8 (2)
O(W6)	0.5772 (2)	-0.3412 (7)	-0.0484 (2)	5.3 (1)
O(W7)	0.5000	-0.5923 (9)	0.0	4.7 (2)

75.5° in 14-bromoflavanone (Cantrell, Stalzer & Becker, 1974), 70.8° in 5,7,14-trimethoxyflavanone (Mariezcurrena, 1978) and 42.2° in 3-bromoflavanone (Cantrell & Hockstein, 1982), but 0.6° in 5,7,13-trihydroxy-14-methoxyflavanone, hesperetin (Shin, Kim & Chun, 1987). The present small dihedral angle in naringin may be due to the crystal packing as described below. The 2,3-dihydropyrone ring takes a flattened 1,2-diplanar conformation with the C(2) and C(3) atoms deviating from the best plane of the benzene ring by 0.141 (8) and -0.121 (13) Å, respectively, and the phenyl ring is attached to the C(2) atom with torsion angle O(1)—C(2)—C(11)—C(12) 18.7 (8)°. The bond distances and angles of the flavanone skeleton in the naringin molecule agree well with those of reported flavanone derivatives (Cantrell & Hockstein, 1982; Cantrell, Stalzer & Becker, 1974; Mariezcurrena, 1978; Shin, Kim & Chun, 1987; Shin & Lah, 1986). An intramolecular hydrogen bond is formed between

* 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 52877 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond distances (Å) and angles (°)

O(1)—C(2)	1.392 (8)	C(1')—C(2')	1.503 (7)
O(1)—C(9)	1.359 (7)	C(1')—O(6')	1.417 (6)
C(2)—C(3)	1.331 (14)	C(2)—O(2)	1.447 (6)
C(2)—C(11)	1.515 (9)	C(2')—C(3')	1.522 (7)
C(3)—C(4)	1.481 (15)	O(2)—C(1'')	1.412 (6)
C(4)—O(4)	1.230 (13)	C(3')—O(3')	1.402 (6)
C(4)—C(10)	1.423 (12)	C(3')—C(4')	1.541 (7)
C(5)—O(5)	1.359 (9)	C(4')—O(4')	1.430 (6)
C(5)—C(6)	1.373 (9)	C(4')—C(5')	1.519 (7)
C(5)—C(10)	1.415 (10)	C(5')—C(6')	1.510 (8)
C(6)—C(7)	1.385 (8)	C(5')—O(6')	1.424 (6)
C(7)—O(7)	1.358 (6)	C(6')—O(7')	1.436 (7)
C(7)—C(8)	1.396 (7)	C(1'')—C(2'')	1.517 (7)
O(7)—C(1')	1.408 (6)	C(2'')—O(6'')	1.418 (6)
C(8)—C(9)	1.371 (8)	C(2'')—O(2'')	1.433 (6)
C(9)—C(10)	1.399 (9)	C(2'')—C(3'')	1.523 (7)
C(11)—C(12)	1.378 (9)	C(3'')—O(3'')	1.447 (7)
C(11)—C(16)	1.389 (9)	C(3'')—C(4'')	1.485 (7)
C(12)—C(13)	1.380 (11)	C(4'')—O(4'')	1.436 (6)
C(13)—C(14)	1.372 (10)	C(4'')—C(5'')	1.535 (7)
C(14)—O(14)	1.421 (9)	C(5'')—C(6'')	1.512 (8)
C(14)—C(15)	1.357 (9)	C(5'')—O(6'')	1.436 (6)
C(15)—C(16)	1.388 (9)		
C(2)—O(1)—C(9)	118.0 (5)	O(7)—C(1')—O(6')	106.1 (4)
O(1)—C(2)—C(3)	122.1 (7)	C(2')—C(1'')—O(6'')	109.2 (4)
O(1)—C(2)—C(11)	109.0 (5)	C(1'')—C(2'')—O(2'')	109.5 (4)
C(3)—C(2)—C(11)	123.9 (8)	C(1'')—C(2'')—C(3'')	109.2 (4)
C(2)—C(3)—C(4)	117.8 (10)	O(2'')—C(2'')—C(3'')	107.9 (4)
C(3)—C(4)—O(4)	122.1 (10)	C(2'')—O(2'')—C(1'')	114.4 (4)
C(3)—C(4)—C(10)	116.0 (8)	C(2'')—C(3'')—O(3'')	111.0 (4)
O(4)—C(4)—C(10)	121.7 (9)	C(2'')—C(3'')—C(4'')	110.3 (4)
O(5)—C(5)—C(6)	118.2 (6)	O(3'')—C(3'')—C(4'')	110.1 (4)
O(5)—C(5)—C(10)	120.0 (6)	C(3'')—C(4'')—O(4'')	109.8 (4)
C(6)—C(5)—C(10)	121.8 (6)	C(3'')—C(4'')—C(5'')	109.7 (4)
C(5)—C(6)—C(7)	118.4 (6)	O(4'')—C(4'')—C(5'')	109.4 (4)
C(6)—C(7)—O(7)	114.6 (5)	C(4'')—C(5'')—C(6'')	111.7 (4)
C(6)—C(7)—C(8)	122.0 (5)	C(4'')—C(5'')—O(6'')	109.6 (4)
O(7)—C(7)—C(8)	123.4 (4)	C(6'')—C(5'')—O(6'')	107.2 (4)
C(7)—O(7)—C(1')	118.2 (4)	C(5'')—C(6'')—O(7')	112.3 (5)
C(7)—C(8)—C(9)	118.3 (5)	C(1')—O(6')—C(5')	112.4 (4)
O(1)—C(9)—C(8)	116.1 (5)	O(2')—C(1'')—C(2'')	107.8 (4)
O(1)—C(9)—C(10)	121.8 (5)	O(2')—C(1'')—O(6'')	111.1 (4)
C(8)—C(9)—C(10)	122.1 (5)	C(2'')—C(1'')—O(6'')	112.5 (4)
C(4)—C(10)—C(5)	122.9 (7)	C(1'')—C(2'')—O(2'')	106.8 (4)
C(4)—C(10)—C(9)	119.8 (7)	C(1'')—C(2'')—C(3'')	109.1 (4)
C(5)—C(10)—C(9)	117.3 (6)	O(2'')—C(2'')—C(3'')	110.0 (4)
C(2)—C(11)—C(12)	121.1 (6)	C(2'')—C(3'')—O(3'')	107.1 (4)
C(2)—C(11)—C(16)	120.5 (6)	C(2'')—C(3'')—C(4'')	112.4 (4)
C(12)—C(11)—C(16)	118.4 (6)	O(3'')—C(3'')—C(4'')	110.5 (4)
C(11)—C(12)—C(13)	121.5 (7)	C(3'')—C(4'')—O(4'')	108.1 (4)
C(12)—C(13)—C(14)	118.5 (7)	C(3'')—C(4'')—C(5'')	110.9 (4)
C(13)—C(14)—O(14)	117.2 (6)	O(4'')—C(4'')—C(5'')	109.3 (4)
C(13)—C(14)—C(15)	122.0 (7)	C(4'')—C(5'')—C(6'')	113.6 (4)
O(14)—C(14)—C(15)	120.7 (6)	C(4'')—C(5'')—O(6'')	108.6 (4)
C(14)—C(15)—C(16)	119.1 (6)	C(6'')—C(5'')—O(6'')	106.7 (4)
C(11)—C(16)—C(15)	120.5 (6)	C(1'')—O(6')—C(5')	114.9 (4)
O(7)—C(1')—C(2')	108.6 (4)		

and C(2'')—O(2''), take axial positions, and three bonds, C(3'')—O(3''), C(4'')—O(4'') and C(5'')—C(6''), adopt equatorial orientations. The rhamnose moiety is connected to the glucose moiety through the O(2') atom with torsion angles C(1')—C(2')—O(2')—C(1'') 134.6 (4) and C(2')—O(2')—C(1'')—C(2'') 156.3 (4)°. The bond distances, angles and endocyclic torsion angles in the glucose and the rhamnose moieties show good agreement with those of previously reported related compounds (Jin, Yamagata & Tomita, 1989; Kanters, Roelofsen, Doesburg & Koops, 1976; Rohrer, Sarko, Bluhm & Lee, 1980).

A stereoview of the crystal packing in the unit cell is illustrated in Fig. 2. All the hydroxyl groups and the water molecules participate in hydrogen bonds. Three intermolecular hydrogen bonds, O(4)⋯O(5) ($1-x, y, 1-z$), O(14)⋯O(4'') ($\frac{1}{2}-x, \frac{1}{2}+y, 1-z$) and O(4'')⋯O(2'') ($\frac{1}{2}-x, \frac{1}{2}+y, -z$), are formed directly between adjacent naringin molecules. Three water molecules are used to connect neighboring naringin

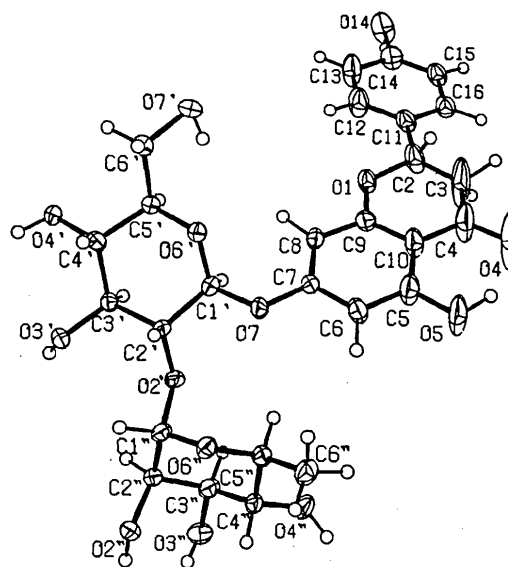


Fig. 1. An ORTEP (Johnson, 1976) plot of a naringin molecule with atom labelling, ellipsoids at 30% probability.

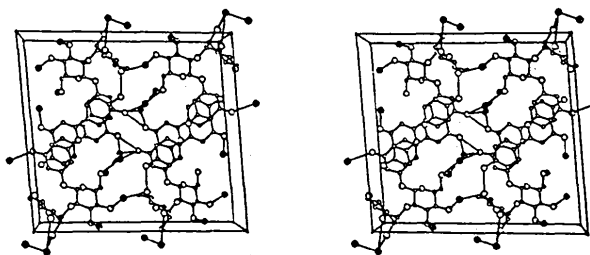


Fig. 2. Stereoscopic drawing of the molecular packing viewed along the *b* axis. The water molecules are shown as solid circles. The thin lines indicate hydrogen bonds.

the carbonyl O(4) atom of the pyranone ring and the hydroxyl O(5) atom of the benzene ring. Similar intramolecular hydrogen bonds are also found in several flavanone and flavone derivatives (Candy, Laing & Weeks, 1975; Estrada, Conde, Marquez & Jimenez-Garay, 1987; Hayashi, Kawai, Ohno, Iitaka & Akimoto, 1974; Jin, Yamagata & Tomita, 1989, 1990; Shin & Lah, 1986; Vijayalakshmi, Rajan & Srinivasan, 1987; Vijayalakshmi, Rajan, Srinivasan & Ramachandran Nair, 1986).

The glucose moiety takes a stable chair form with the equatorial orientation of all exocyclic bonds and is linked to the benzene ring through the O(7) atom with torsion angles C(6)—C(7)—O(7)—C(1')—176.9 (5) and C(7)—O(7)—C(1')—C(2')—165.3 (4)°. The rhamnose moiety also adopts a stable chair form, while two exocyclic bonds, O(2'')—C(1'')

molecules through hydrogen bonds, O(5)···O(W2)···O(7')($-\frac{1}{2} + x, -\frac{1}{2} + y, z$), O(3')···O(W3)···O(3')($\frac{3}{2} - x, -\frac{1}{2} + y, -z$) and O(4')···O(W4)···O(4')($\frac{1}{2} + x, \frac{1}{2} + y, z$). The water O(W7) molecule located on the twofold axis forms hydrogen bonds to the O(6'') atoms of the rhamnose moiety and to the water O(W6) molecules. As a characteristic feature of the crystal packing, a widely spread intermolecular stacking interaction with a separation of about 3.68 Å is observed between two nearly planar 4-hydroxyphenylbenzopyranone groups which are related by a twofold screw axis as shown in Fig. 2.

This work was partly supported by a Grant-in-Aid from the Tokyo Biochemical Research Foundation.

References

- CANDY, H. A., LAING, M. & WEEKS, C. M. (1975). *Tetrahedron Lett.* **14**, 1211–1214.
- CANTRELL, J. S. & HOCKSTEIN, G. S. (1982). *Acta Cryst.* **B38**, 981–983.
- CANTRELL, J. S., STALZER, R. A. & BECKER, T. L. (1974). *Acta Cryst.* **B30**, 154–161.
- ESTRADA, M. D., CONDE, A., MARQUEZ, R. & JIMENEZ-GARAY, R. (1987). *Acta Cryst.* **C43**, 1826–1829.
- HAYASHI, T., KAWAI, S., OHNO, T., IITAKA, Y. & AKIMOTO, T. (1974). *Chem. Pharm. Bull.* **22**, 1219–1226.
- International Tables for X-ray Crystallography* (1974). Vol. IV, pp. 72–75. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
- JIN, G. Z., YAMAGATA, Y. & TOMITA, K. (1989). *Chem. Pharm. Bull.* In the press.
- JIN, G. Z., YAMAGATA, Y. & TOMITA, K. (1990). *Acta Cryst.* **C46**, 310–313.
- JOHNSON, C. K. (1976). *ORTEP*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
- KANTERS, J. A., ROELOFSEN, G., DOESBURG, H. M. & KOOPS, T. (1976). *Acta Cryst.* **B32**, 2830–2837.
- MARIEZCURRENA, R. A. (1978). *Acta Cryst.* **B34**, 2322–2324.
- ROHRER, D. C., SARKO, A., BLUHM, T. L. & LEE, Y. N. (1980). *Acta Cryst.* **B36**, 650–654.
- SHELDRICK, G. M. (1986). *SHELX86*. Program for the solution of crystal structures. Univ. of Göttingen, Federal Republic of Germany.
- SHIN, W., KIM, S. & CHUN, K. S. (1987). *Acta Cryst.* **C43**, 1946–1949.
- SHIN, W. & LAH, M. S. (1986). *Acta Cryst.* **C42**, 626–628.
- UNICS (1979). *Universal Crystallographic Computation Program System*. The Crystallographic Society of Japan, Tokyo, Japan.
- VARMA, S. D. & KINOSHITA, J. H. (1976). *Biochem. Pharmacol.* **25**, 2505–2513.
- VIJAYALAKSHMI, J., RAJAN, S. S. & SRINIVASAN, R. (1987). *Acta Cryst.* **C43**, 1998–2000.
- VIJAYALAKSHMI, J., RAJAN, S. S., SRINIVASAN, R. & RAMACHANDRAN NAIR, A. G. (1986). *Acta Cryst.* **C42**, 1752–1754.

Acta Cryst. (1990). **C46**, 1869–1872

Structures of (2*R*,4*S*,5*R*)-3,4-Dimethyl-2,5-diphenyl-1,3,2-oxazaphospholidine(*P*-*B*)borane (1) and of (2*R*,5*S*)-5-Methyl-2,4,4-triphenyl-1,3,2-dioxaphospholane(*P*-*B*)borane (2)

BY S. JUGÉ, M. STEPHAN AND J. P. GENET

Laboratoire de Synthèse Organique, Ecole Nationale Supérieure de Chimie de Paris, 11 rue Pierre et Marie Curie, 75231 Paris, France

AND S. HALUT-DESSPORTES AND S. JEANNIN

Laboratoire de Chimie des Métaux de Transition, UA 419 Université Pierre et Marie Curie, 4 Place Jussieu 75232 Paris, France

(Received 30 October 1989; accepted 14 December 1989)

Abstract. Compound (1): C₁₆H₂₁BNOP, m.p. = 383 K, *M_r* = 285.1, monoclinic, *P*2₁, *a* = 10.570 (5), *b* = 7.796 (1), *c* = 10.409 (1) Å, β = 107.74 (1)°, *V* = 816.9 (8) Å³, *Z* = 2, *D_m* = 1.158 (floatation in tetrachloromethane–hexane), *D_x* = 1.159 Mg m⁻³, λ(Mo *K*α) = 0.71070 Å, μ = 0.157 mm⁻¹, *F*(000) = 304, *T* = 294 K, *R* = 0.037, *wR* = 0.036 for 1104 significant reflections. Absolute configuration *R* of P atom deduced from known *R* configuration of C(5) and *S* configuration of C(4). Compound (2): C₂₁H₂₂BO₂P, m.p. = 431 K, *M_r* = 348.2, monoclinic,

*P*2₁, *a* = 17.261 (4), *b* = 10.509 (5), *c* = 10.689 (1) Å, β = 96.73 (1)°, *V* = 1926 (2) Å³, *Z* = 4, *D_m* = 1.199 (floatation in tetrachloromethane–hexane), *D_x* = 1.201 Mg m⁻³, μ(Mo *K*α) = 0.147 mm⁻¹, *F*(000) = 736, *T* = 294 K, *R* = 0.049, *wR* = 0.058 for 3361 significant reflections. Absolute configuration *R* of P atom deduced from known *S* configuration of C(4) atom.

Introduction. The *trans* isomers of 2-phenyl-1,3,2-oxazaphospholidine and 1,3,2-dioxaphospholane are