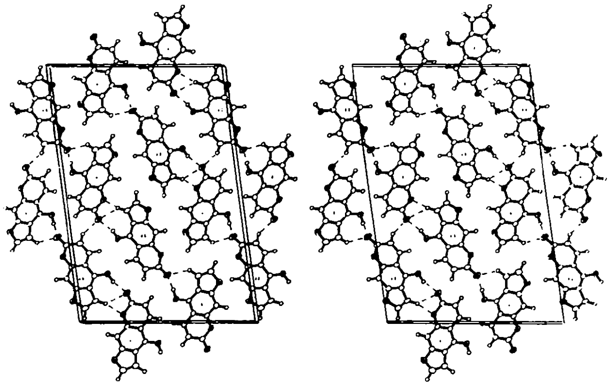

Fig. 2. Représentation stéréoscopique des chaînes de molécules $C_{11}H_6O_4$ suivant **b**. Les liaisons hydrogène sont représentées par des traits interrompus.

tivement identiques et de 3,39 Å; ce qui est comparable aux valeurs trouvées pour le psoralène ($C_{11}H_6O_3$) de 3,41 Å (Bideau, Bravic & Desvergne, 1979) et pour d'autres coumarines substituées (Shimizu, Kashino & Haisa, 1975).

Les distances OH···O sont de 2,719 et de 2,736 Å. De même que dans le cas de la coumarine, $C_9H_6O_2$ (Gavuzzo & Mazza, 1974), c'est l'atome d'oxygène du groupement carboxyle qui contribue le plus à la cohésion cristalline.

L'auteur remercie Messieurs A. Valla et M. Giraud du Laboratoire de Chimie Appliquée aux Corps Organisés du Muséum National d'Histoire Naturelle de lui avoir proposé l'étude de cette molécule et fourni les cristaux.

Références

Bideau, J. P., Bravic, G. & Desvergne, J. P. (1979). *Cryst. Struct. Commun.* **8**, 695–698.

Busing, W. R., Martin, K. O. & Levy, H. A. (1962). *ORFLS*. Rapport ORNL-TM-305. Oak Ridge National Laboratory, Tennessee, EU.

Gavuzzo, E. & Mazza, F. (1974). *Acta Cryst.* B**30**, 1351–1357.

Johnson, C. K. (1976). *ORTEP*II. Rapport ORNL-5138. Oak Ridge National Laboratory, Tennessee, EU.

Martin, M. T., Valla, A., Giraud, M., Brouard, J. P., Morlière, P., Haigle, J. & Santus, R. (1991). *Photochem. Photobiol.* Soumis.

Marzulli, F. N. & Mailbach, H. I. (1970). *J. Soc. Cosmet. Chem.* **21**, 942.

Parrish, J. A., White, H. A. D., Pathak, M. A., Fitzpatrick, T. B., Eissen, A. Z., Wolf, K., Freedberg, I. M. & Austen, K. F. (1979). *Photomedicine in Dermatology in General Medicine*, pp. 942–994. New York: McGraw-Hill.

Sheldrick, G. M. (1986). *SHELXS*86. Programme pour la résolution de structures cristallines. Univ. de Göttingen, Allemagne.

Shimizu, S., Kashino, S. & Haisa, M. (1975). *Acta Cryst.* B**31**, 1287–1292.

Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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(*RS*)-2-(*p*-Benzyloxyphenyl)-2-methyl-3,4,5,6-tetrahydro-2*H*-pyran-3-one

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Abstract. $C_{19}H_{20}O_3$, $M_r = 296{\cdot}37$, monoclinic, $P2_1/c$, $a = 9{\cdot}983\ (2)$, $b = 17{\cdot}076\ (4)$, $c = 9{\cdot}575\ (2)$ Å, $\beta = 99{\cdot}95\ (2)°$, $V = 1607{\cdot}7\ (6)$ Å^3, $Z = 4$, $D_x = 1{\cdot}22$ Mg m^{-3}, $\lambda(\mathrm{Cu}\ K\alpha) = 1{\cdot}5418$ Å, $\mu = 0{\cdot}576$ mm^{-1}, $F(000) = 632$, room temperature, $R = 0{\cdot}056$ for 2367 unique reflections $[I > 3\sigma(I)]$. The pyranoid ring has a chair conformation distorted towards a half chair.

Introduction. As a part of studies on the conformation of sugars with one *sp*^{2}-hybridized C atom in the pyranoid ring by X-ray diffraction methods, several pyranosides with the C_{sp^2} atom in a vicinal position to the anomeric center of the pyranoid ring have been investigated (Palmer & Palmer, 1976; Smiatacz, Myszka & Ciunik, 1988; Ciunik, Paulsen, Luger, Smiatacz & Myszka, 1989). The main aim of this work was the determination of the conformation of the pyranoid ring in the absence of the OAc and/or NHAc side groups in positions 3 and 4 of the ring.

Experimental. The title compound was prepared and crystallized as previously reported (Georgiadis, Haroutounian & Bailar, 1988). Crystal dimensions

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Table 1. *Final positional and thermal parameters* ($\times 10^4$) *with e.s.d.'s in parentheses*

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}(Å^2)
O(1)	2934 (2)	6104 (1)	7166 (2)	671 (4)
O(2)	714 (2)	7458 (1)	5357 (2)	853 (5)
O(3)	2614 (2)	4667 (1)	933 (2)	642 (4)
C(1)	3462 (3)	7166 (2)	5809 (4)	807 (8)
C(2)	2458 (2)	6498 (1)	5853 (2)	531 (4)
C(3)	1013 (2)	6825 (1)	5835 (2)	546 (4)
C(4)	52 (3)	6306 (2)	6424 (4)	795 (7)
C(5)	706 (4)	5951 (2)	7817 (4)	875 (8)
C(6)	2006 (3)	5551 (2)	7628 (3)	788 (7)
C(7)	2433 (2)	5963 (1)	4572 (2)	482 (4)
C(8)	1783 (2)	6194 (1)	3232 (2)	572 (5)
C(9)	1855 (2)	5749 (1)	2049 (2)	603 (5)
C(10)	2584 (2)	5054 (1)	2175 (2)	518 (4)
C(11)	3227 (2)	4807 (1)	3498 (2)	541 (4)
C(12)	3150 (2)	5266 (1)	4681 (2)	533 (4)
C(13)	3418 (3)	3968 (1)	975 (3)	652 (6)
C(14)	3352 (2)	3710 (1)	− 523 (2)	548 (5)
C(15)	4435 (2)	3856 (1)	− 1229 (3)	610 (5)
C(16)	4375 (3)	3640 (1)	− 2614 (3)	652 (6)
C(17)	3240 (3)	3271 (1)	− 3339 (3)	685 (6)
C(18)	2156 (3)	3119 (2)	− 2658 (3)	748 (6)
C(19)	2212 (2)	3340 (1)	− 1260 (3)	669 (6)

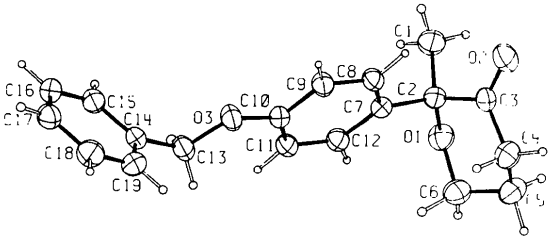

Fig. 1. *ORTEP* drawing of the molecule with crystallographic numbering scheme. The ellipsoids correspond to 30% probability contours of atomic displacement.

Table 2. *Bond lengths* (Å), *valence and selected torsion angles* (°) *with e.s.d.'s in parentheses*

O(1)—C(2)	1·433 (3)	C(7)—C(12)	1·383 (3)
O(1)—C(6)	1·445 (4)	C(8)—C(9)	1·376 (3)
O(2)—C(3)	1·191 (2)	C(9)—C(10)	1·386 (3)
O(3)—C(10)	1·365 (3)	C(10)—C(11)	1·383 (3)
O(3)—C(13)	1·435 (3)	C(11)—C(12)	1·390 (3)
C(1)—C(2)	1·524 (4)	C(13)—C(14)	1·491 (4)
C(2)—C(3)	1·544 (3)	C(14)—C(15)	1·393 (3)
C(2)—C(7)	1·526 (3)	C(14)—C(19)	1·384 (3)
C(3)—C(4)	1·487 (4)	C(15)—C(16)	1·368 (4)
C(4)—C(5)	1·507 (5)	C(16)—C(17)	1·375 (4)
C(5)—C(6)	1·505 (5)	C(17)—C(18)	1·381 (5)
C(7)—C(8)	1·391 (3)	C(18)—C(19)	1·383 (4)

C(2)—O(1)—C(6)	116·3 (2)	C(7)—C(8)—C(9)	121·4 (2)
C(10)—O(3)—C(13)	118·3 (2)	C(8)—C(9)—C(10)	120·2 (2)
O(1)—C(2)—C(1)	104·8 (2)	O(3)—C(10)—C(9)	115·4 (2)
O(1)—C(2)—C(3)	110·3 (2)	O(3)—C(10)—C(11)	125·0 (2)
O(1)—C(2)—C(7)	112·4 (2)	C(9)—C(10)—C(11)	119·6 (2)
C(1)—C(2)—C(3)	110·3 (2)	C(10)—C(11)—C(12)	119·5 (2)
C(1)—C(2)—C(7)	110·2 (2)	C(7)—C(12)—C(11)	121·6 (2)
C(3)—C(2)—C(7)	108·8 (2)	O(3)—C(13)—C(14)	106·7 (2)
O(2)—C(3)—C(2)	120·3 (2)	C(13)—C(14)—C(15)	120·3 (2)
O(2)—C(3)—C(4)	123·5 (2)	C(13)—C(14)—C(19)	121·4 (2)
C(2)—C(3)—C(4)	116·3 (2)	C(15)—C(14)—C(19)	118·2 (2)
C(3)—C(4)—C(5)	111·5 (3)	C(14)—C(15)—C(16)	121·0 (2)
C(4)—C(5)—C(6)	109·1 (3)	C(15)—C(16)—C(17)	120·5 (2)
O(1)—C(6)—C(5)	110·6 (3)	C(16)—C(17)—C(18)	119·5 (3)
C(2)—C(7)—C(8)	120·8 (2)	C(17)—C(18)—C(19)	120·1 (3)
C(2)—C(7)—C(12)	121·2 (2)	C(14)—C(19)—C(18)	120·7 (2)
C(8)—C(7)—C(12)	117·8 (2)		

O(1)—C(2)—C(3)—O(2)	139·0 (2)	O(1)—C(2)—C(3)—C(4)	− 41·6 (3)
O(1)—C(2)—C(7)—C(12)	− 17·0 (3)	O(1)—C(6)—C(5)—C(4)	59·7 (3)
O(2)—C(3)—C(2)—C(1)	23·7 (3)	O(2)—C(3)—C(4)—C(5)	− 134·5 (3)
O(3)—C(13)—C(14)—C(19)	− 76·5 (3)	C(1)—C(2)—O(1)—C(6)	166·9 (2)
C(1)—C(2)—C(3)—C(4)	− 156·9 (2)	C(1)—C(2)—C(7)—C(8)	− 74·9 (2)
C(2)—O(1)—C(6)—C(5)	− 59·5 (3)	C(2)—C(3)—C(4)—C(5)	46·1 (3)
C(2)—C(7)—C(8)—C(9)	174·2 (2)	C(3)—C(2)—O(1)—C(6)	48·1 (2)
C(3)—C(2)—C(7)—C(8)	46·1 (2)	C(3)—C(4)—C(5)—C(6)	− 53·7 (4)
C(6)—O(1)—C(2)—C(7)	− 73·5 (2)	C(10)—O(3)—C(13)—C(14)	− 175·6 (2)
C(11)—C(10)—O(3)—C(13)	− 2·9 (3)		

0·2 × 0·2 × 0·3 mm; space group determined from oscillation and Weissenberg photographs (D_m was not measured), room temperature, Kuma KM4 κ-axis computer-controlled four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation. Unit-cell dimensions from least-squares refinement of the setting angles of 25 reflections ($30 \leq 2\theta \leq 45°$). 2θ range 4–150°, ω–2θ scan method, h −12–12, k 0–21, l 0–11, variable scan width $\Delta\omega = (1{\cdot}6 + 0{\cdot}35\tan\theta)°$ and scan rate 1·2–6° min^{-1}. Data were corrected for Lorentz and polarization effects, but not for absorption. Three check reflections [intensity variation less than $3\sigma(I)$]. Of the 3738 measured reflections (3071 unique, $R_{\rm int} = 0{\cdot}021$), 2367 reflections with $F > 6\sigma(F)$ were used in the analysis. The structure was solved by direct methods and subjected to full-matrix anisotropic least-squares refinement on F. H atoms were indentified in difference syntheses and refined freely with isotropic temperature factors. The final R value was 0·056, with $wR = 0{\cdot}070$. The weighting scheme was $w^{-1} = \sigma^2(F) + 0{\cdot}004F^2$. 280 parameters (including isotropic secondary-extinction parameter $x = 0{\cdot}006$); max. Δ/σ 0·039; min. and max. $\Delta\rho$ −0·25 and 0·17 e Å^{-3}, respectively. The final atomic parameters are given in Table 1.* All computations were performed using *SHELXS*86 (Sheldrick, 1986), *SHELX*76 (Sheldrick, 1976), *ORTEP* (Johnson, 1971) and *PUCK*2 (Luger & Bülow, 1983). Scattering factors were those in *SHELX*76.

Discussion. The molecular scheme and the overall conformation are shown in Fig. 1 Coordinates given in Table 1 correspond to the S enantiomer. Table 2 lists bond distances and angles, and selected torsion angles.

The pyranoid ring has the $^2C_5$ chair conformation. The Cremer & Pople (1975) ring-puckering parameters [$Q = 0{\cdot}519$ (3) Å, $\theta = 167{\cdot}1$ (3) and $\varphi = 91$ (1)°]

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* Lists of structure factors, anisotropic temperature factors, H-atom parameters, interatomic distances and valence angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 54122 (30 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

indicate some distortion towards the $^5H_6$ half chair with O(1)—C(6)—C(5)—C(4) and O(1)—C(2)—C(3)—C(4) torsion angles 59·7 (3) and −41·6 (3)°, respectively. Similar deformations were observed in carbohydrates with the sp^2-hybridized C atom in position 2 of the pyranoid ring. The distortion in the title compound corresponds to a small deformation of the chair conformation (Ciunik, Szweda & Smiatacz, 1991).

The benzyloxyphenyl group is an axial substitutent (2*a*) of the pyranoid ring and the O(1)—C(2)—C(7)—C(12) torsion angle is −17·0 (3)°. In consequence the pyranoid and the aromatic rings are almost perpendicular to each other. The benzyloxyphenyl substituent has the extended antiperiplanar conformation with C(10)—O(3)—C(13)—C(14) and C(11)—C(10)—O(3)—C(13) torsion angles of −175·6 (2) and −2·9 (3)°, respectively. Both aromatic rings are mutually twisted. All bond lengths and valence angles have normal values.

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References

Ciunik, Z., Paulsen, H., Luger, P., Smiatacz, Z. & Myszka, H. (1989). *Acta Cryst.* **B45**, 512–518.

Ciunik, Z., Szweda, R. & Smiatacz, Z. (1991). *Carbohydr. Res.* In the press.

Cremer, D. & Pople, J. A. (1975). *J. Am. Chem. Soc.* **97**, 1354–1358.

Georgiadis, M. P., Haroutounian, S. A. & Bailar, J. C. Jr (1988). *J. Heterocycl. Chem.* **25**, 995–1002.

Johnson, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

Luger, P. & Bülow, R. (1983). *J. Appl. Cryst.* **16**, 431–432.

Palmer, H. T. & Palmer, R. A. (1976). *Acta Cryst.* **B32**, 377–380.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.

Sheldrick, G. M. (1986). *SHELXS86*. Program for the solution of crystal structures. Univ. of Göttingen, Germany.

Smiatacz, Z., Myszka, H. & Ciunik, Z. (1988). *Carbohydr. Res.* **172**, 171–182.

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Temperature Effect on the Structure of the Complex 1,8-Bis(dimethylamino)naphthalene–Chloranilic Acid* (2/1) Dihydrate

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Abstract. $2C_{14}H_{18}N_2.C_6H_2Cl_2O_4.2H_2O$, M_r = 673·64, triclinic, $P\bar{1}$, $Z = 1$, λ(Mo $K\alpha$) = 0·71073 Å, μ = 2·5 cm^{-1}, $F(000) = 356$. Cell dimensions at 150 K: a = 9·3051 (7), b = 9·3261 (4), c = 9·5779 (8) Å, α = 104·604 (5), β = 98·486 (6), γ = 92·913 (5)°, V = 792·1 (1) Å^3, D_x = 1·412 g cm^{-3}, R = 0·040 for 3343 reflections with $I \geq 2{\cdot}5\sigma(I)$. At 295 K: a = 9·420 (3), b = 9·444 (3), c = 9·626 (3) Å, α = 104·84 (4), β = 97·84 (4), γ = 92·66 (4)°, V = 817·1 (5) Å^3, D_x = 1·369 g cm^{-3}, R = 0·036 for 2426 reflections with $I \geq 3{\cdot}0\sigma(I)$. The structure consists of centrosymmetric doubly ionized chloranilic acid anions and protonated bis(dimethylamino)naphthalene cations. The water molecules act as cohesive elements by connecting the anions through hydrogen bonds to form endless chains which run in the **a** direction. The channels formed by these chains accommodate pairs of centrosymmetrically related cations. The intramolecular NHN$^+$ hydrogen bonds in the cation with distances of 2·589 (3) (at 295 K) and 2·588 (2) Å (at 150 K) are asymmetric and nonlinear. The asymmetry, which is caused by the interaction with the chloranilate anion, increases on cooling.

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* 2,5-Dichloro-3,6-dihydroxy-*p*-benzoquinone.

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