

final difference Fourier synthesis were $0.28 \text{ e } \text{Å}^{-3}$, located 1.13 Å from O(1), and $-0.37 \text{ e } \text{Å}^{-3}$, located at a distance of 0.67 Å from C(6) and 0.69 Å from O(6). Calculations were performed on Hitachi AS XL 60 and PDP 11/34 computers. Atomic scattering factors were those of *SHELX*. The refined atomic and isotropic thermal parameters are listed in Table 1.* Interatomic distances and bond angles for the non-H atoms are presented in Table 2, while hydrogen-bonding contacts are summarized in Table 3. The atom-labelling scheme of the hypoxanthinium cation is shown in Fig. 1. Fig. 2 represents the packing diagram of hypoxanthinium nitrate monohydrate.

Related literature. The changes in the ring geometry of different purine derivatives as a result of protonation at an N atom have been reviewed by Taylor & Kennard (1982). The major influence observed is an increase of the corresponding C—N—C angle of about $3\text{--}4^\circ$ upon protonation. The molecular dimensions of the N(1)-, N(7)- and N(9)-protonated hypoxanthinium cation described here are in good agreement with the corresponding values in hypoxanthine hydrochloride monohydrate (Sletten &

Jensen, 1969) and also with the data reported for hypoxanthine gold(III) tetrachloride dihydrate (Caira, Nassimbeni & Rodgers, 1975). A comparison of the bond angles of neutral hypoxanthine (Schmalle, Hänggi & Dubler, 1988), where the H atoms are attached at the N atoms N(1) and N(9), with those of the cation indicates that protonation at the N(7) atom induces an increase of the angle C(5)—N(7)—C(8) from a mean value of $104.2 (1)^\circ$ in hypoxanthine to $108.4 (2)^\circ$ in the hypoxanthinium cation. The geometry of neutral hypoxanthine involved in metal-complex formation has recently been discussed (Dubler, Hänggi & Bensch, 1987; Dubler, Hänggi & Schmalle, 1987)

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52251 (14 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

- CAIRA, M. R., NASSIMBENI, L. R. & RODGERS, A. L. (1975). *Acta Cryst.* **B31**, 1112–1115.
 DUBLER, E., HÄNGGI, G. & BENSCH, W. (1987). *J. Inorg. Biochem.* **29**, 269–288.
 DUBLER, E., HÄNGGI, G. & SCHMALLE, H. (1987). *Acta Cryst.* **C44**, 1872–1875.
 JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
 ROSENSTEIN, R. D., OBERDING, M., HYDE, J. R., ZUBIETA, J., KARLIN, K. D. & SEEMAN, N. C. (1982). *Cryst. Struct. Commun.* **11**, 1507–1513.
 SCHMALLE, H. W., HÄNGGI, G. & DUBLER, E. (1988). *Acta Cryst.* **C44**, 732–736.
 SHELDRICK, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.
 SLETTEN, J. & JENSEN, L. H. (1969). *Acta Cryst.* **B25**, 1608–1614.
 TAYLOR, R. & KENNARD, O. (1982). *J. Mol. Struct.* **78**, 1–28.

Acta Cryst. (1990). **C46**, 342–344

Structure of the Lignane (+)-Pinoresinol Dimethyl Ether

BY MARTA VASQUEZ, FRANK R. FRONCZEK AND NIKOLAUS H. FISCHER

Department of Chemistry, Louisiana State University, Baton Rouge, Louisiana 70803, USA

(Received 13 September 1988; accepted 31 July 1989)

Abstract. $\text{C}_{22}\text{H}_{26}\text{O}_6$, $M_r = 386.4$, orthorhombic, $P2_12_12_1$, $a = 9.250 (4)$, $b = 12.311 (2)$, $c = 17.603 (2) \text{ Å}$, $V = 2004.5 (10) \text{ Å}^3$, $Z = 4$, $D_x = 1.280 \text{ g cm}^{-3}$, $\text{Cu K}\alpha$, $\lambda = 1.54184 \text{ Å}$, $\mu = 7.2 \text{ cm}^{-1}$, $F(000) = 824$, $T = 298 \text{ K}$, $R = 0.038$ for 1733 observations (of 2350 unique data). The two five-membered rings of the central dioxabicyclooctane system are *cis*-fused, each ring adopting the half-chair conformation with one atom lying on both pseudodiads. The phenyl rings are planar within maximum deviation $0.011 (3) \text{ Å}$, and the four methoxy substituents lie near these planes, with CCOC torsion angles in the range $1.7 (4)\text{--}6.5 (4)^\circ$.

Experimental. The compound was isolated from *Rudbeckia maxima* Nutt., *R. nitida* Perdue and *R. scabrifolia* Brown (Asteraceae) which were collected in Alto, Texas, East Baton Rouge Parish, Louisiana, and Vernon Parish, Louisiana, respectively. Pinoresinol dimethyl ether (1) was obtained as colorless needles, one with dimensions $0.15 \times 0.28 \times 0.45 \text{ mm}$ was mounted in a capillary because of the failure of the epoxy glue to harden properly in the presence of this compound. Space group from absences $h00$ with h odd, $0k0$ with k odd, $00l$ with l odd. Enraf–Nonius CAD-4 diffractometer with graphite monochromator, cell dimensions from

Table 1. Positional and equivalent isotropic thermal parameters and their e.s.d.'s

$$B_{\text{eq}} = (8\pi^2/3) \sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	x	y	z	$B_{\text{eq}}(\text{\AA}^2)$
C1	0.2462 (3)	0.7726 (2)	0.4361 (1)	3.82 (6)
C2	0.3640 (3)	0.7382 (2)	0.4913 (1)	3.76 (6)
O3	0.4005 (3)	0.6302 (2)	0.4694 (1)	4.89 (5)
C4	0.4037 (4)	0.6324 (3)	0.3884 (2)	5.19 (8)
C5	0.2882 (3)	0.7139 (2)	0.3625 (1)	3.90 (6)
C6	0.3454 (4)	0.8041 (2)	0.3098 (1)	4.04 (6)
O7	0.3585 (3)	0.8985 (2)	0.3567 (1)	5.24 (5)
C8	0.2508 (4)	0.8920 (2)	0.4147 (2)	5.11 (7)
C9	0.3259 (3)	0.7416 (2)	0.5748 (1)	3.49 (5)
C10	0.2745 (3)	0.6499 (2)	0.6120 (1)	3.68 (6)
C11	0.2360 (3)	0.6545 (2)	0.6883 (1)	3.54 (6)
C12	0.2469 (3)	0.7533 (2)	0.7275 (1)	3.69 (6)
C13	0.2975 (3)	0.8434 (2)	0.6910 (2)	4.29 (7)
C14	0.3383 (4)	0.8372 (2)	0.6149 (2)	4.46 (7)
O15	0.1872 (3)	0.5680 (2)	0.72985 (9)	4.58 (5)
C16	0.1678 (5)	0.4679 (2)	0.6911 (2)	6.02 (9)
O17	0.2027 (2)	0.7496 (2)	0.80229 (9)	4.49 (5)
C18	0.2267 (5)	0.8466 (3)	0.8458 (2)	6.27 (9)
C19	0.2570 (4)	0.8271 (2)	0.2389 (1)	3.70 (6)
C20	0.3294 (3)	0.8392 (2)	0.1701 (1)	3.73 (6)
C21	0.2542 (4)	0.8612 (2)	0.1039 (1)	3.94 (6)
C22	0.1047 (3)	0.8746 (2)	0.1064 (1)	4.02 (6)
C23	0.0332 (3)	0.8632 (3)	0.1746 (2)	4.63 (7)
C24	0.1096 (4)	0.8387 (3)	0.2401 (2)	4.78 (7)
O25	0.3158 (3)	0.8732 (2)	0.0332 (1)	5.69 (5)
C26	0.4676 (4)	0.8653 (3)	0.0281 (2)	5.97 (9)
O27	0.0398 (3)	0.9000 (2)	0.0385 (1)	5.18 (5)
C28	-0.1112 (4)	0.9196 (4)	0.0398 (2)	7.2 (1)

setting angles of 25 reflections having $24 > \theta > 19^\circ$. Data collection by ω - 2θ scans designed for $I = 50\sigma(I)$, subject to max. scan time = 120 s. Scan rates varied 0.53 – $3.30^\circ \text{ min}^{-1}$. Reflections having $4 < 2\theta < 150^\circ$, $0 \leq h \leq 11$, $0 \leq k \leq 15$, $0 \leq l \leq 22$ measured, corrected for background, Lorentz-polarization and absorption by ψ scans, minimum relative transmission 0.9596, 2350 unique data, no redundant data. Standard reflections 200, 020, 002, $\pm 2.3\%$ maximum random variation, no decay correction. Structure solved using *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978), refinement by full-matrix least squares based on F with weights $w = 4F_o^2[\sigma^2(I) + (0.02F_o^2)^2]^{-1}$ with 1733 data for which $I > 2.5\sigma(I)$ (617 unobserved reflections), using Enraf-Nonius *SDP* (Frenz & Okaya, 1980). Non-H atoms anisotropic; H atoms located by ΔF synthesis and included as fixed contributions. Isotropic B 's were assigned to H atoms, equal to $1.3 B_{\text{eq}}$ of the bonded C atoms. Positions of methyl H atoms were adjusted using ΔF maps, while other H-atom positions were calculated with C—H 0.95 Å. Atomic scattering factors of Cromer & Waber (1974) and anomalous coefficients of Cromer (1974). Final $R = 0.03806$ (0.066 all data), $wR = 0.04105$, $S = 1.989$ for 254 variables, extinction coefficient $g = 1.57(10) \times 10^{-6}$, where the correction factor $(1 + gI_c)^{-1}$ was applied to F_o , max. shift in final cycle 0.03σ , max. residual density 0.13 , min. -0.14 e \AA^{-3} . Refinement

Table 2. Bond distances (Å), angles ($^\circ$) and selected torsion angles ($^\circ$)

C1	C2	1.519 (3)	C11	C12	1.401 (3)				
C1	C5	1.534 (3)	C11	O15	1.368 (2)				
C1	C8	1.518 (3)	C12	C13	1.365 (3)				
C2	O3	1.425 (3)	C12	O17	1.380 (2)				
C2	C9	1.513 (3)	C13	C14	1.393 (3)				
O3	C4	1.426 (2)	O15	C16	1.421 (3)				
C4	C5	1.534 (3)	O17	C18	1.436 (3)				
C5	C6	1.541 (3)	C19	C20	1.392 (3)				
C6	O7	1.431 (3)	C19	C24	1.371 (4)				
C6	C19	1.519 (3)	C20	C21	1.384 (3)				
O7	C8	1.428 (3)	C21	C22	1.393 (3)				
C9	C10	1.389 (3)	C21	O25	1.376 (2)				
C9	C14	1.377 (3)	C22	C23	1.377 (3)				
C10	C11	1.391 (3)	C22	O27	1.373 (2)				
C23	C24	1.386 (3)	O27	C28	1.418 (4)				
O25	C26	1.410 (3)							
C2	C1	C5	103.1 (2)	C6	O7	C8	107.9 (2)		
C2	C1	C8	114.1 (2)	C1	C8	O7	104.6 (2)		
C5	C1	C8	103.8 (2)	C2	C9	C10	121.0 (2)		
C1	C2	O3	104.9 (2)	C2	C9	C14	120.2 (2)		
C1	C2	C9	116.5 (2)	C10	C9	C14	118.8 (2)		
O3	C2	C9	110.1 (2)	C9	C10	C11	120.6 (2)		
C2	O3	C4	104.9 (2)	C10	C11	C12	119.9 (2)		
O3	C4	C5	107.1 (2)	C10	C11	O15	124.7 (2)		
C1	C5	C4	103.5 (2)	C12	C11	O15	115.8 (2)		
C1	C5	C6	104.9 (2)	C11	C12	C13	119.9 (2)		
C4	C5	C6	114.3 (2)	C11	C12	O17	114.8 (2)		
C5	C6	O7	105.5 (2)	C13	C12	O17	125.3 (2)		
C5	C6	C19	116.4 (2)	C12	C13	C14	120.1 (2)		
O7	C6	C19	111.6 (2)	C9	C14	C13	121.1 (2)		
C11	O15	C16	117.4 (2)	C22	C21	O25	115.3 (2)		
C12	O17	C18	115.8 (2)	C21	C22	C23	119.5 (2)		
C6	C19	C20	118.4 (2)	C21	C22	O27	115.7 (2)		
C6	C19	C24	122.8 (2)	C23	C22	O27	124.8 (2)		
C20	C19	C24	118.8 (2)	C22	C23	C24	120.2 (2)		
C19	C20	C21	120.8 (2)	C19	C24	C23	121.1 (2)		
C20	C21	C22	119.7 (2)	C21	O25	C26	117.6 (2)		
C20	C21	O25	125.0 (2)	C22	O27	C28	117.1 (2)		
C5	C1	C2	O3	-33.3 (3)	O3	C4	C5	C1	11.7 (3)
C5	C1	C2	C9	-155.4 (3)	O3	C4	C5	C6	125.2 (3)
C8	C1	C2	O3	-145.2 (3)	C1	C5	C6	O7	10.1 (3)
C8	C1	C2	C9	92.7 (3)	C1	C5	C6	C19	-114.3 (3)
C2	C1	C5	C4	12.7 (3)	C4	C5	C6	O7	-102.6 (3)
C2	C1	C5	C6	-107.4 (3)	C5	C6	O7	C8	-30.2 (3)
C8	C1	C5	C4	132.0 (3)	C19	C6	O7	C8	97.1 (3)
C8	C1	C5	C6	11.9 (3)	C5	C6	C19	C20	-134.8 (3)
C2	C1	C8	O7	81.5 (3)	C6	O7	C8	C1	38.3 (3)
C5	C1	C8	O7	-30.0 (3)	C10	C11	O15	C16	-3.3 (4)
C1	C2	O3	C4	41.9 (3)	C11	C12	O17	C18	173.8 (3)
C9	C2	O3	C4	168.0 (3)	C22	C21	O25	C26	177.2 (3)
C2	O3	C4	C5	-33.4 (3)	C21	C22	O27	C28	-176.9 (3)

of the enantiomorphous structure yielded $R = 0.03820$, $wR = 0.04116$, $S = 1.994$. Atomic coordinates and equivalent isotropic thermal parameters for the former refinement are given in Table 1,* bond distances, angles and endocyclic torsion angles describing the conformation in Table 2. Fig. 1 shows the atom-numbering scheme. The title compound has $[\alpha]_D^{20^\circ} = +60.9^\circ$ [CHCl_3 , 5.0 g dm^{-3}] while the literature value (Erdtman, 1935) is $+64.4^\circ$.

* Tables of H-atom parameters, anisotropic thermal parameters and structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52159 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

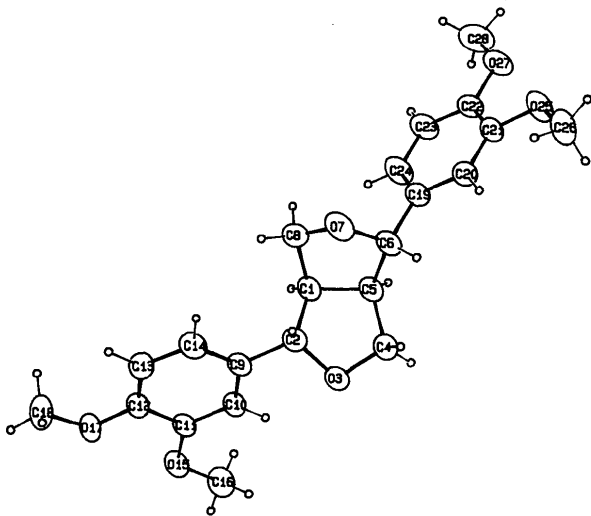


Fig. 1. Numbering scheme and thermal ellipsoids drawn at the 40% probability level. H atoms are represented by circles of arbitrary radius.

Related literature. Description of lignanes (Haworth, 1936); synthesis of (+), (-) and (\pm) forms of pinoresinol dimethyl ether (Erdtman, 1936); reaction with bromine to yield dibromo derivatives (Erdtman, 1935); characterization of lignanes having a 2,6-diaryl-*cis*-3,7-dioxabicyclo[3.3.0]octane structure (Adjangba, 1963; Hearon & MacGregor, 1955); unit-cell and space-group determination of dibromo and diiodo derivatives of pinoresinol dimethyl ether, establishing twofold molecular symmetry (Wang Lund, 1960); crystal-structure determination of the lignane (-)-syringaresinol (Bryan & Fallon, 1976),

crystal-structure determination of the lignane (-)-3,6-bis(3,4-dimethoxyphenyl)tetrahydro-1*H*,3*H*-furo[3,4-*c*]furan-1,4-diol (Ghisalberti, Jefferies, Skelton & White, 1987).

This research was supported by the Louisiana Education Quality Support Fund (86-89)-RD-A-13 and the National Science Foundation Biotechnology Program (project No. EET-8713078). The purchase of the diffractometer was made possible by an NSF instrumentation grant (CHE-8500781).

References

- ADJANGBA, M. S. (1963). *Bull. Soc. Chim. Fr.* pp. 2344-2358.
 BRYAN, R. F. & FALLON, L. (1976). *J. Chem. Soc. Perkin Trans. 1*, pp. 341-345.
 CROMER, D. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.3.1. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 CROMER, D. T. & WABER, J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2B. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)
 ERDTMAN, H. (1935). *Justus Liebigs Ann. Chem.* **513**, 229-239.
 ERDTMAN, H. (1936). *Sven. Kem. Tidskr.* **48**, 236-241.
 FRENZ, B. A. & OKAYA, Y. (1980). *Enraf-Nonius Structure Determination Package*. Enraf-Nonius, Delft, The Netherlands.
 GHISALBERTI, E. L., JEFFERIES, P. R., SKELTON, B. W. & WHITE, A. H. (1987). *Aust. J. Chem.* **40**, 405-411.
 HAWORTH, R. D. (1936). *Annu. Rep. Prog. Chem.* **33**, 266-279.
 HEARON, W. M. & MACGREGOR, W. S. (1955). *Chem. Rev.* **55**, 957-1068.
 MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 WANG LUND, E. (1960). *Acta Chem. Scand.* **14**, 496-497.

Acta Cryst. (1990). **C46**, 344-346

Structure of the Perchlorate Salt of Hetsine 13-*O*-Acetate

BY JOHN F. RICHARDSON* AND MICHAEL H. BENN

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

(Received 4 August 1989; accepted 25 September 1989)

Abstract. $C_{22}H_{30}NO_4^+ \cdot ClO_4^-$, $M_r = 471.94$, orthorhombic, $P2_12_12_1$, $a = 11.835(1)$, $b = 15.736(1)$, $c = 11.342(1)$ Å, $V = 2112.4(4)$ Å³, $Z = 4$, $D_x = 1.48$ Mg m⁻³, Mo $K\alpha$, $\lambda = 0.7107$ Å, $\mu = 0.24$ mm⁻¹, $F(000) = 1000$, $T = 294$ K, final $R =$

0.055 for 1841 reflections. The perchlorate salt of this hitherto unknown 13-*O*-acetyl derivative of the alkaloid hetsine was examined to confirm the gross structure and relative configuration.

Experimental. Colourless plate, 0.15 × 0.30 × 0.50 mm, Enraf-Nonius CAD-4F diffractometer, graphite-monochromated Mo $K\alpha$ radiation; lattice

* Present address: Department of Chemistry, University of Louisville, Louisville, Kentucky 40292, USA.