forms a six-membered ring between the γ-butyrolactone and the trimethoxybenzene ring in normal phenyltetrahydronaphthalene-type lignans.

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Reinvestigation of the Structure of Hypoxanthinium Nitrate Monohydrate

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Abstract. $C_5H_5N_4O^+.NO_3^-.H_2O$, $M_r = 217·14$, orthorhombic, *Pnma*, $a = 13·699\ (3)$, $b = 6·264\ (4)$, $c = 10·069\ (2)$ Å, $V = 864·0$ Å^3, $Z = 4$, $D_x = 1·669$ g cm^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 1·02$ cm^{-1}, $F(000) = 448$, room temperature, $R = 0·054$ for 1154 observed reflections. As part of our investigations on metal–hypoxanthine complexes, the structure of hypoxanthine nitrate monohydrate was redetermined in order to provide more reliable data on protonated hypoxanthine for structural comparison purposes. The reinvestigation, confirming the general structural features of the compound reported by Rosenstein, Oberding, Hyde, Zubieta, Karlin & Seeman [*Cryst. Struct. Commun.* (1982), **11**, 1507–1513] resulted in bond distances and angles with e.s.d.'s of 0·003 Å and 0·2° for the hypoxanthinium cation and of 0·002 Å and 0·2° for the nitrate group. These e.s.d.'s are smaller by a factor of about seven compared with the values reported by Rosenstein *et al.* (1982), which had been obtained by a refinement based on 253 observed reflections only. In addition, the reinvestigation of the structure yielded new positions for the water H atoms and some significant differences in the positions of the hypoxanthine H atoms. Since all H atoms were localized in difference Fourier maps and successfully refined, the existence of N(1)-, N(7)- and N(9)-protonated hypoxanthinium cations, nitrate anions and non-protonated water molecules could be confirmed. The hypoxanthinium and the nitrate ions are planar due to unit-cell symmetry. Each hypoxanthinium cation is surrounded by three different nitrate groups and *vice versa*, forming layers perpendicular to the *b* axis of the cell with an interplanar spacing of $b/2 = 3·132\ (4)$ Å. This layered structure is stabilized by an extended hydrogen-bonding system. The H atoms H(1), H(7) and H(9) of the hypoxanthinium ion are involved in hydrogen bonds of the type N—H···O with the adjacent nitrate groups, whereas the water molecules are hydrogen bonded to N(3) and O(6) of the hypoxanthinium cation and to O(1) of the nitrate group. The hydrogen bonds involving H(1) and H(42) are bifurcated. Despite the pronounced layer-type structure of the compound, no direct purine–purine stacking is observed. In contrast, the nitrate groups are stacked approximately on top of each other rotated by about 180°, forming infinite columns along the *b* axis of the cell.

Experimental. Single crystals of hypoxanthinium nitrate monohydrate were prepared by dissolving 200 mg (1·47 mmol) hypoxanthine in 120 ml 2·5*M* HNO_3 at 370 K. After crystallization for 3 weeks at room temperature, needle-shaped crystals suitable for X-ray investigations could be isolated from this solution. Composition: calculated C 27·66, H 3·25, N 32·25%; observed C 27·87, H 3·52, N 32·52%.

A transparent crystal with dimensions 0·72 × 0·25 × 0·21 mm was mounted along its needle axis (*b*) on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. The lattice constants were derived from least-squares

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Table 1. *Positional and thermal parameters*

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

	x	y	z	U_{eq}/U_{iso} (Å^2)
N(1)	0·6234 (2)	0·2500	1·2515 (2)	0·0463 (6)
C(2)	0·5406 (2)	0·2500	1·1780 (3)	0·0464 (7)
N(3)	0·5375 (1)	0·2500	1·0482 (2)	0·0435 (5)
C(4)	0·6284 (2)	0·2500	0·9952 (2)	0·0361 (5)
C(5)	0·7147 (2)	0·2500	1·0607 (2)	0·0353 (5)
C(6)	0·7181 (2)	0·2500	1·2007 (2)	0·0394 (6)
O(6)	0·7892 (1)	0·2500	1·2753 (2)	0·0546 (5)
N(7)	0·7870 (2)	0·2500	0·9673 (2)	0·0418 (5)
C(8)	0·7459 (2)	0·2500	0·8482 (3)	0·0462 (7)
N(9)	0·6493 (2)	0·2500	0·8620 (2)	0·0440 (6)
N	0·5325 (2)	0·2500	1·5698 (2)	0·0499 (6)
O(1)	0·6224 (1)	0·2500	1·5575 (2)	0·0684 (6)
O(2)	0·4938 (1)	0·2500	1·6812 (2)	0·0605 (6)
O(3)	0·4799 (1)	0·2500	1·4688 (2)	0·0582 (6)
O(4)	0·3422 (1)	0·2500	0·9317 (2)	0·0528 (5)
H(1)	0·6138 (19)	0·2500	1·3457 (28)	0·067 (9)
H(2)	0·4777 (20)	0·2500	1·2294 (24)	0·073 (10)
H(7)	0·8528 (18)	0·2500	0·9876 (25)	0·059 (9)
H(8)	0·7807 (21)	0·2500	0·7564 (26)	0·083 (10)
H(9)	0·6031 (20)	0·2500	0·8102 (30)	0·075 (11)
H(41)	0·4064 (24)	0·2500	0·9608 (32)	0·104 (13)
H(42)	0·3048 (24)	0·2500	1·0023 (31)	0·104 (14)

Table 2. *Interatomic bond distances* (Å) *and angles* (°)

N(1)—C(2)	1·354 (3)	C(5)—N(7)	1·367 (3)
C(2)—N(3)	1·308 (3)	N(7)—C(8)	1·325 (3)
N(3)—C(4)	1·354 (3)	C(8)—N(9)	1·330 (3)
C(4)—C(5)	1·354 (3)	N(9)—C(4)	1·372 (3)
C(5)—C(6)	1·410 (3)	C(6)—O(6)	1·230 (3)
C(6)—N(1)	1·394 (3)		
N—O(1)	1·239 (2)	N—O(3)	1·246 (2)
N—O(2)	1·240 (2)		
C(6)—N(1)—C(2)	125·4 (2)	N(7)—C(8)—N(9)	109·2 (2)
N(1)—C(2)—N(3)	124·9 (3)	C(8)—N(9)—C(4)	108·1 (2)
C(2)—N(3)—C(4)	111·3 (2)	N(9)—C(4)—C(5)	107·1 (2)
N(3)—C(4)—C(5)	127·7 (2)	N(3)—C(4)—N(9)	125·3 (2)
C(4)—C(5)—C(6)	121·0 (2)	C(6)—C(5)—N(7)	131·7 (2)
C(5)—C(6)—N(1)	109·6 (2)	N(1)—C(6)—O(6)	120·9 (2)
C(4)—C(5)—N(7)	107·3 (2)	C(5)—C(6)—O(6)	129·5 (2)
C(5)—N(7)—C(8)	108·4 (2)		
O(1)—N—O(2)	121·0 (2)	O(2)—N—O(3)	119·4 (2)
O(1)—N—O(3)	119·5 (2)		

Table 3. *Hydrogen-bonding contacts* (Å,°)

X—H···Y	X—H	H···Y	X···Y	X—H···Y
N(1)—H(1)···O(1)	0·96 (3)	2·14 (3)	3·081 (3)	169 (2)
N(1)—H(1)···O(3)	0·96 (3)	2·21 (3)	2·942 (3)	132 (2)
N(7)—H(7)···O(3)	0·92 (3)	1·80 (3)	2·719 (3)	179 (2)
N(9)—H(9)···O(2)	0·82 (3)	1·98 (3)	2·802 (3)	178 (3)
O(4)—H(41)···N(3)	0·93 (3)	2·00 (3)	2·921 (3)	172 (3)
O(4)—H(42)···O(6)	0·88 (3)	2·25 (3)	3·038 (3)	150 (3)
O(4)—H(42)···O(1)	0·88 (3)	2·57 (3)	3·013 (3)	112 (3)

refinement of 25 centred reflections in the interval 10 < θ < 14°. Intensities were collected in the interval 1 < θ < 40° using the ω–2θ scan technique with variable scan speeds between 1·8 and 5·5° min^{-1}. The index range was $0 \leq h \leq 24$, $-11 \leq k \leq 11$, $0 \leq l \leq 18$. Three standard reflections measured every 3 h showed no significant decrease of intensities. To control orientation three standard reflections were collected every 200 reflections. Data reduction ($R_{\rm int}$ = 0·016 for 2936 averaged reflections) led to 2360 unique reflections. The data were corrected for Lorentz and polarization effects, and a numerical absorption correction, based on nine carefully indexed crystal faces, was applied (min. and max. transmission factors are 0·967 and 0·982 respectively).

The atomic coordinates determined by Rosenstein, Oberding, Hyde, Zubieta, Karlin & Seeman (1982) were used in a starting set of full-matrix least-squares calculations. Anisotropic refinements were carried out with *SHELX76* (Sheldrick, 1976) by minimizing $\sum w(|F_o| - |F_c|)^2$ with $w = K/\sigma^2(F_o)$ (K = 6·56). All H atoms could be localized in the difference Fourier maps and were refined with variable positional and variable isotropic temperature factors. Reflections 002 and 013 were omitted because secondary extinction was suspected. Final refinement using 1154 reflections with $I \geq 3\sigma(I)$ and 112 variable parameters converged with a maximum final shift-to-e.s.d. ratio of 0·03 to R = 0·054 and wR = 0·037. The maximum and minimum electron densities in the

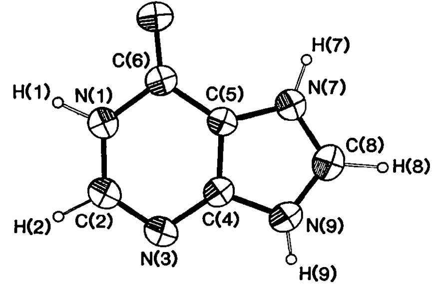

Fig. 1. *ORTEP* (Johnson, 1971) drawing of the hypoxanthinium cation showing the atom-labelling scheme. Thermal ellipsoids are scaled to enclose 50% probability.

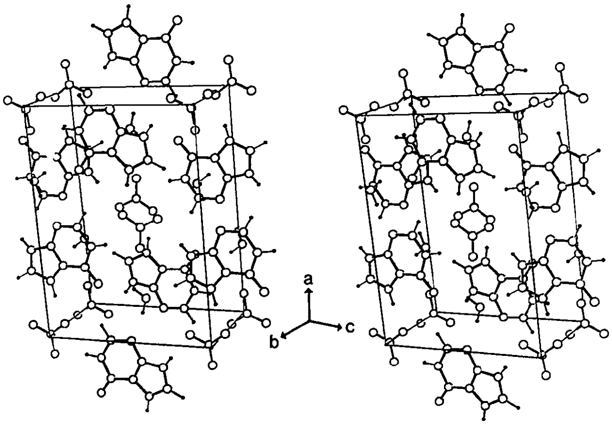

Fig. 2. *ORTEP* (Johnson, 1971) stereo plot of the packing diagram of hypoxanthinium nitrate monohydrate.

final difference Fourier synthesis were 0·28 e Å^{-3}, located 1·13 Å from O(1), and −0·37 e 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 3–4° 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)° in hypoxanthine to 108·4 (2)° 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)

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* 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.

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Structure of the Lignane (+)-Pinoresinol Dimethyl Ether

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Abstract. $C_{22}H_{26}O_6$, $M_r = 386·4$, orthorhombic, $P2_12_12_1$, $a = 9·250\ (4)$, $b = 12·311\ (2)$, $c = 17·603\ (2)$ Å, $V = 2004·5\ (10)$ Å^3, $Z = 4$, $D_x = 1·280$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1·54184$ Å, $\mu = 7·2$ cm^{-1}, $F(000) = 824$, $T = 298$ 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) Å, and the four methoxy substituents lie near these planes, with CCOC torsion angles in the range 1·7 (4)–6·5 (4)°.

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 × 0·28 × 0·45 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

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