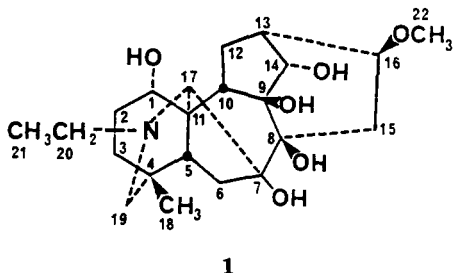# X-RAY INVESTIGATION OF TATSININE PERCHLORATE

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Previous communications (1,2) from this laboratory have described the isolation and characterization of three novel and six known diterpenoid alkaloids from the roots of the Chinese larkspur, *Delphinium tatsienense* Franch. Among the new alkaloids, the structure of tatsinine (**1**) was deduced from biogenetic

1

We decided to confirm the postulated structure of **1** by X-ray analysis because of the complexity of the structure elucidation and the alkaloid's unusual substitution pattern.

Initial investigation of tatsinine was unsuccessful because of crystal imperfections, so the perchlorate salt was prepared and was found suitable for crystallographic analysis. The reported structure of tatsinine was verified. Table 1 lists the fractional coordinates for the perchlorate of **1**.[1] Figure 1 depicts an ORTEP view of the molecule.

Interestingly, the crystal exists in a highly disordered state and was found to incorporate solvent of crystallization.
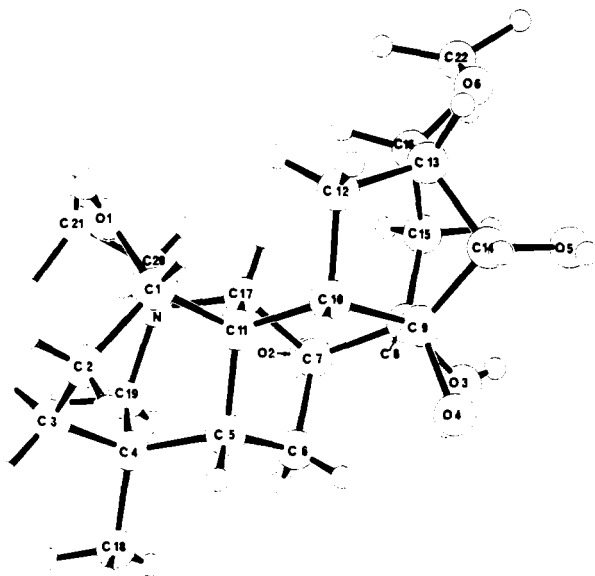
FIGURE 1. An ORTEP drawing of tatsinine (**1**).

considerations and elaborate spectral analysis and is particularly interesting. Tatsinine (**1**) is very polar and possesses a series of four vicinal hydroxyl groups, as well as a fifth, isolated hydroxy group.
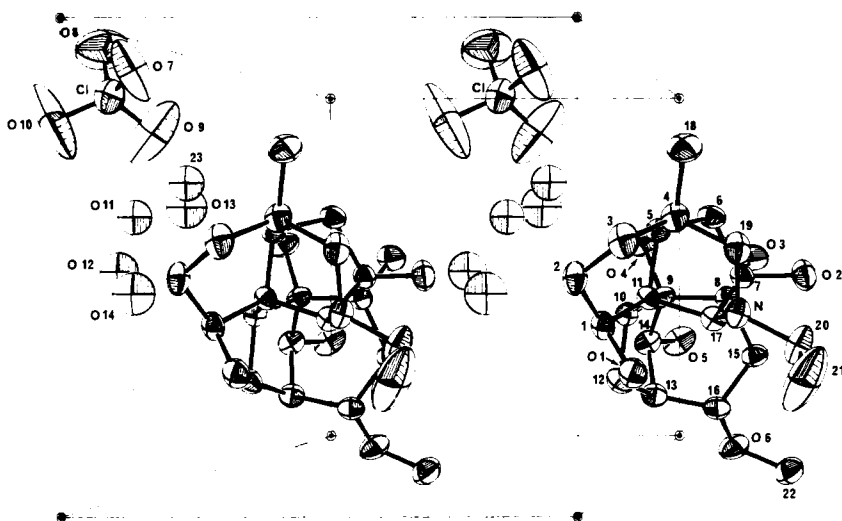
FIGURE 2.   Tatsinine perchlorate assymmetric unit.

The alkaloid and its counterion delimit a large channel, illustrated in the ORTEP view of the unit cell (Figure 2), in which several sites are available for solvent occupancy. In addition to MeOH, three intense peaks within the channel were assumed to be H_2O, in accord with the polarity of the sample and hygroscopicity of the crystal. Because of the proximity of some of the solvent atoms, the crystal was modeled as having several partially occupied potential sites for solvent of crystallization. This description proved very satisfactory and converged, yielding a MeOH-H_2O ratio of 0.588:0.412 at one locus, and another H_2O molecule split between two additional sites in the ratio 0.599:0.401. Despite the solvent presence, no hydrogen bonding or other unusual intermolecular contacts were observed. The oxygen atoms of the perchlorate anion, and all solvent atoms, possess large thermal amplitudes.

The conformation of tatsinine perchlorate is not unusual; the disordered solvent makes the structure interesting, however. Normally, C_{19}-type diterpenoid alkaloids bearing a C(1)-α-OH exist with the A-ring in a boat conformation to facilitate hydrogen bonding between the hydroxyl and nitrogen atom. In the present case, even though the nitrogen is protonated in the salt, the A-ring assumes a twisted boat form with an oxygen lone pair apparently oriented toward the ammonium hydrogen.

EXPERIMENTAL

A colorless crystal of tatsinine perchlorate, $C_{22}H_{35}NO_6 \cdot HClO_4$, mp 132-133° (corrected), dimensions 0.20×0.25×0.30 mm, was selected. All measurements were carried out on an Enraf-Nonius CAD4 diffractometer system using CuKα radiation ($\lambda = 1.5418$Å) with an $\omega/2\theta$ scan technique (for 5°<θ<75°) and a variable scan speed. The scan width was (0.8+0.14 tan θ)° plus 25% on either side for background. Unit cell parameters were determined by least-squares fit of 25 strong reflections (23°<θ<37°) and yielded a=8.7129(2), b=8.3948(2), c=18.0520(3)Å, $\alpha = \gamma = 90$°, $\beta = 103.13(3)$°, and V=1287.6Å^3. For z=2 the computed density was 1.32 g/cm^3. Examination of systematic extinctions indicated that the monoclinic crystal belonged to space group P2$_1$. Of the 3026 reflections measured, 2648 were unique and 2461 of these had I>3σ (I) and were used in the least-squares refinement. The quantity minimized during refinement was w|ΔF|^2, where w= 1/σ(F)^2.

The structure was solved by multisolution methods (3), using the program MULTAN (4), and refined by a full-matrix least-squares method. Prior to incorporation of solvent of crystallization all nonhydrogen atoms were located, with R converging to 0.152; hydrogens refused to refine properly. A difference Fourier map revealed a molecule of MeOH, and a subsequent e-map revealed the presence of H_2O. These solvent molecules, and all hydrogen atoms, were refined with fixed isotropic temperature factors. Occu-

TABLE 1.   Fractional Atomic Coordinates and Their Estimated Standard Deviations

Atom	x	y	z	B(A2)
CL1	0.6069(2)	0.953	0.3284(1)	5.37(4)
O4	0.9214(4)	0.5648(5)	0.0979(2)	3.16(7)
O2	1.3802(4)	0.4773(5)	0.2624(2)	3.54(7)
C2	0.8107(5)	0.4716(8)	0.3737(3)	3.4(1)
C7	1.2141(5)	0.4751(6)	0.2393(2)	2.52(8)
O3	1.2264(4)	0.5271(5)	0.1124(2)	3.54(7)
O6	1.1703(4)	−0.0171(5)	0.0965(2)	3.64(7)
O1	0.9566(1)	0.2232(5)	0.3748(2)	3.62(7)
C10	0.8965(5)	0.3684(6)	0.1925(2)	2.36(8)
C5	1.0026(5)	0.5982(6)	0.2889(2)	2.48(8)
C1	0.8686(5)	0.3443(7)	0.3266(2)	2.76(8)
C11	0.9734(5)	0.4170(6)	0.2751(2)	2.23(7)
C9	0.9794(5)	0.4140(6)	0.1283(2)	2.44(8)
C16	1.1313(6)	0.1011(6)	0.1461(3)	2.78(8)
C8	1.1626(5)	0.4129(6)	0.1554(2)	2.53(8)
C4	1.0633(15)	0.6294(7)	0.3757(3)	3.03(9)
C18	1.0898(7)	0.8074(8)	0.3922(3)	4.5(1)
C13	0.9545(6)	0.1333(6)	0.1191(3)	2.84(9)
C14	0.9246(6)	0.2812(7)	0.0696(2)	2.80(8)
C15	1.2357(5)	0.2487(6)	0.1463(3)	2.76(8)
C6	1.1344(6)	0.6369(6)	0.2470(3)	2.79(8)
C17	1.1456(5)	0.3615(6)	0.2906(2)	2.42(8)
N1	1.2212(4)	0.3794(6)	0.3746(2)	2.74(7)
C19	1.2238(6)	0.5487(8)	0.4019(3)	3.3(1)
C3	0.9451(6)	0.5678(8)	0.4214(4)	3.8(1)
C12	0.8757(6)	0.1824(7)	0.1834(3)	3.00(9)
C20	1.3778(6)	0.2988(9)	0.4006(3)	4.5(1)
C22	1.3266(7)	−0.0812(87)	0.1218(4)	4.2(1)
O5	1.0003(5)	0.2797(5)	0.0079(2)	3.83(7)
O7	0.7121(6)	1.009(1)	0.3948(3)	9.1(2)
O8	0.5541(9)	1.0862(9)	0.2811(4)	9.0(2)
C21	1.395(1)	0.219(2)	0.4715(5)	9.9(3)
O9	0.4752(8)	0.885(1)	0.3435(5)	14.6(3)
O10	0.688(1)	0.862(1)	0.2850(6)	14.0(3)
C23	0.662(2)	0.739(2)	0.1143(7)	5.8(3)*
O13	0.621(1)	0.674(2)	0.0515(7)	8.5(3)*
O11	0.574(1)	0.640(2)	0.1948(7)	5.5(2)*
O12	0.392(1)	0.489(1)	−0.0004(6)	7.6(2)*
O14	0.455(2)	0.422(3)	0.0298(1)	9.3(5)*

*These atoms were refined isotropically.

pancy refinement was conducted for a MeOH/ H_2O pair (separation 2.0Å) and another H_2O pair (separation 0.8Å). Subsequently, hydrogens were located stereochemically (except for solvent) and were well-behaved. Final R (R_w) was 0.056 (0.075), and another difference map revealed no significant peaks.

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