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### (*S*)-1-Acetoxymethyl-2-acetyl-1,2,3,4-tetrahydro-6,7-dimethoxy-1-methylisoquinoline

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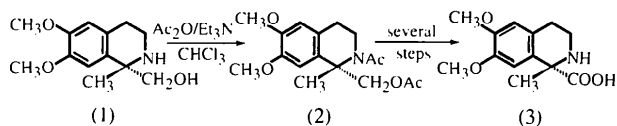
#### Abstract

The title compound [(*S*)-2-acetyl-1,2,3,4-tetrahydro-6,7-dimethoxy-1-methyl-1-isoquinolinylmethyl acetate, C<sub>17</sub>H<sub>23</sub>NO<sub>5</sub>] is a key chiral intermediate in the synthesis of some natural isoquinoline derivatives with a C1 quaternary centre. This diacetyl derivative has been proposed as a stable intermediate storage compound. The absolute structure has been verified.

#### Comment

In the course of our first enantioselective synthesis (Czarnocki, Suh, MacLean, Hultin & Szarek, 1992) of mammalian alkaloid (Collins, 1983), we prepared (*S*)-1,2,3,4-tetrahydro-1-hydroxymethyl-6,7-dimethoxy-1-methylisoquinoline, (1), as a key synthetic intermediate. This amino alcohol proved to be quite unstable, especially in solution. In order to avoid its extensive decomposition during storage, we decided to transform it into the title diacetyl derivative, (2), which appears to be indefinitely stable and may be transformed back into the parent amino alcohol by basic hydrolysis. A further synthetic sequence led to the synthesis of (*S*)-1,2,3,4-tetrahydro-6,7-dimethoxy-1-methylisoquinoline-1-carboxylic acid, (3), as a final product. The absolute stereochemistry of this compound was established by

comparison with the results obtained by Chrzanowska, Schonenberger, Brossi & Flippen-Anderson (1987) for (*S*)-salsoline-1-carboxylic acid. In this report, we describe the X-ray crystal structure and absolute configuration of (2).



The optical purity of (2) is greater than 95%, as indicated by chiral HPLC (Czarnocki *et al.*, 1992), and the absolute configuration was confirmed as the expected *S* by refinement of the Flack (1983) enantiopole parameter to 0.14 (24). The C5–C10 aromatic ring is planar (r.m.s. deviation = 0.012 Å). The methoxy groups at the C6 and C7 atoms are slightly rotated around the C6–O4 and C7–O5 bonds (Fig. 1), the dihedral angles between the plane of the aromatic ring and the planes defined by atoms C6, O4, C17 and C7, O5, C18 being 15.7 (3) and 11.0 (3)°, respectively. The C4 atom lies almost in the plane of the aromatic ring, whereas atom C1 is slightly displaced from it [the deviations of atoms C4 and C1 from the ring plane are 0.028 (4) and –0.095 (3) Å, respectively]. Atoms C11 and C12, bonded to the chiral C1 atom, lie in the plane almost perpendicular to the mean plane of both rings, with the dihedral angle between the plane of the aromatic ring and the plane defined by atoms C11, C1 and C12 being 89.7 (1)°. The acetyl group at the N atom is planar (r.m.s. deviation = 0.004 Å) and only slightly rotated from the ‘best plane’ of both condensed rings (r.m.s. deviation = 0.200 Å), whereas the planar acetoxy group at the C11 atom (r.m.s. deviation = 0.000 Å) is almost

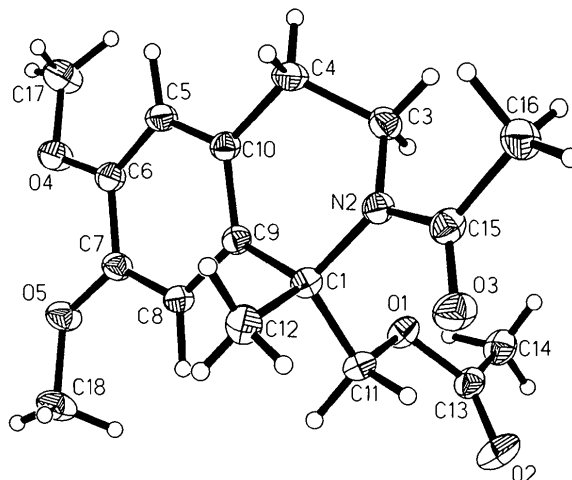


Fig. 1. The molecular structure of the title compound showing the atom-numbering scheme and 30% probability ellipsoids for non-H atoms.

perpendicular to it [the dihedral angles between the 'best plane' and the planes of the acetyl and acetoxy groups are 15.2 (1) and 84.5 (1)°, respectively].

### Experimental

A sample of 0.537 g (2.25 mmol) of 1,2,3,4-tetrahydro-1-hydroxymethyl-6,7-dimethoxy-1-methylisoquinoline, (1), was dissolved in 40 ml of dichloromethane and 3.0 ml of triethylamine was added. After cooling to 283 K, 2.0 ml of freshly distilled acetic anhydride was slowly introduced *via* a syringe. After the addition was complete, the solution was stirred at room temperature for 3 h. All volatile materials were then evaporated and the residue was taken up into 20 ml of toluene. The organic layer was washed twice with a saturated solution of sodium bicarbonate and water. After drying with anhydrous magnesium sulfate, the solvent was evaporated and the residue chromatographed over silica gel (230–400 mesh, Merck) using 1% methanol in chloroform as eluent. Evaporation of the solvent afforded (*S*)-1-acetoxymethyl-2-acetyl-1,2,3,4-tetrahydro-6,7-dimethoxy-1-methylisoquinoline, (2), as a crystalline product in 87% yield. M.p. 407–409 K;  $[\alpha]_D^{23} -17.22^\circ$  (c 2.09, CHCl<sub>3</sub>); <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, δ, TMS): 1.78 (s, 3H), 1.83 (s, 3H), 2.23 (s, 3H), 2.80 (m, 2H), 3.65 (m, 2H), 3.86 (s, 3H), 3.87 (s, 3H), 4.67 and 5.25 (AB quartet, *J* = 11.2 Hz, 2H), 6.57 (s, 1H), 6.74 p.p.m. (s, 1H); <sup>13</sup>C NMR (50.3 MHz, CDCl<sub>3</sub>, δ, TMS): 20.76, 24.38, 25.59, 30.13, 45.24, 55.86, 56.15, 61.92, 68.19, 109.19, 110.50, 128.24, 131.99, 147.51, 147.96, 170.24, 170.57 p.p.m.

### Crystal data

C<sub>17</sub>H<sub>23</sub>NO<sub>5</sub>

*M<sub>r</sub>* = 321.36

Monoclinic

*P*2<sub>1</sub>

*a* = 8.0060 (10) Å

*b* = 12.097 (2) Å

*c* = 8.7940 (10) Å

β = 101.120 (10)°

*V* = 835.7 (2) Å<sup>3</sup>

*Z* = 2

*D<sub>x</sub>* = 1.277 Mg m<sup>-3</sup>

*D<sub>m</sub>* not measured

Cu Kα radiation

λ = 1.54178 Å

Cell parameters from 25

reflections

θ = 20–25°

μ = 0.775 mm<sup>-1</sup>

*T* = 293 (2) K

Plate

0.5 × 0.4 × 0.2 mm

Colourless

### Data collection

KUMA KM-4 κ-axis four-circle diffractometer

Profile data from θ–ω scans

Absorption correction: none

1972 measured reflections

1874 independent reflections

1583 observed reflections

[*I* > 2σ(*I*)]

*R*<sub>int</sub> = 0.0274

θ<sub>max</sub> = 84.95°

*h* = -10 → 10

*k* = -15 → 0

*l* = -11 → 0

3 standard reflections

monitored every 200

reflections

intensity decay: none

### Refinement

Refinement on *F*<sup>2</sup>

*R*(*F*) = 0.0355

*wR*(*F*<sup>2</sup>) = 0.1024

*S* = 1.033

1874 reflections

Extinction correction:

*SHELXL93* (Sheldrick,

1993)

Extinction coefficient:

0.050 (4)

301 parameters

All H-atom parameters

refined

$$w = 1/[\sigma^2(F_o^2) + (0.0747P)^2 + 0.0354P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

$$(\Delta/\sigma)_{\max} = -0.001$$

$$\Delta\rho_{\max} = 0.165 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.150 \text{ e } \text{Å}^{-3}$$

Atomic scattering factors

from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Absolute configuration:

Flack (1983) parameter

$$= 0.14 (24)$$

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (Å<sup>2</sup>)

$$U_{eq} = (1/3)\sum_i \sum_j U_{ij} a_i^* a_j^* a_i \cdot a_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i> <sub>eq</sub>
O1	0.2750 (2)	0.2492 (2)	-0.1412 (2)	0.0522 (4)
O2	0.0681 (3)	0.2410 (3)	-0.3487 (2)	0.0845 (7)
O3	0.0534 (2)	-0.0039 (2)	0.0053 (2)	0.0688 (5)
O4	0.7198 (2)	0.4925 (2)	0.4305 (3)	0.0728 (6)
O5	0.4218 (2)	0.55886 (15)	0.3068 (3)	0.0655 (5)
N2	0.3105 (2)	0.07306 (15)	0.0903 (2)	0.0470 (4)
C1	0.2409 (3)	0.1848 (2)	0.1127 (2)	0.0439 (4)
C3	0.4933 (3)	0.0644 (2)	0.1024 (3)	0.0560 (5)
C4	0.5830 (3)	0.1077 (2)	0.2567 (3)	0.0581 (6)
C5	0.6519 (3)	0.3018 (2)	0.3515 (3)	0.0522 (5)
C6	0.6121 (3)	0.4124 (2)	0.3591 (3)	0.0534 (5)
C7	0.4520 (3)	0.4490 (2)	0.2886 (3)	0.0492 (5)
C8	0.3387 (3)	0.3757 (2)	0.2062 (2)	0.0459 (4)
C9	0.3788 (3)	0.2631 (2)	0.1941 (2)	0.0424 (4)
C10	0.5357 (3)	0.2266 (2)	0.2702 (2)	0.0464 (4)
C11	0.1525 (3)	0.2307 (2)	-0.0447 (2)	0.0490 (5)
C12	0.1091 (4)	0.1773 (3)	0.2173 (3)	0.0581 (6)
C13	0.2139 (3)	0.2552 (2)	-0.2938 (2)	0.0534 (5)
C14	0.3465 (4)	0.2808 (3)	-0.3827 (3)	0.0677 (7)
C15	0.2071 (3)	-0.0138 (2)	0.0400 (3)	0.0528 (5)
C16	0.2848 (4)	-0.1260 (3)	0.0306 (4)	0.0707 (7)
C17	0.8903 (4)	0.4657 (4)	0.4688 (6)	0.0898 (13)
C18	0.2563 (4)	0.5969 (3)	0.2606 (5)	0.0759 (9)

Table 2. Selected geometric parameters (Å, °)

O1—C13	1.339 (2)	C1—C12	1.531 (3)
O1—C11	1.433 (3)	C1—C11	1.532 (3)
O2—C13	1.186 (3)	C3—C4	1.502 (4)
O3—C15	1.215 (3)	C4—C10	1.498 (3)
O4—C6	1.367 (3)	C5—C6	1.380 (3)
O4—C17	1.380 (4)	C5—C10	1.395 (3)
O5—C7	1.366 (3)	C6—C7	1.385 (3)
O5—C18	1.387 (3)	C7—C8	1.371 (3)
N2—C15	1.358 (3)	C8—C9	1.408 (3)
N2—C3	1.450 (3)	C9—C10	1.377 (3)
N2—C1	1.490 (3)	C13—C14	1.468 (4)
C1—C9	1.524 (3)	C15—C16	1.503 (4)
C13—O1—C11	116.3 (2)	O5—C7—C8	125.2 (2)
C6—O4—C17	116.9 (2)	O5—C7—C6	115.4 (2)
C7—O5—C18	118.0 (2)	C8—C7—C6	119.4 (2)
C15—N2—C3	120.8 (2)	C7—C8—C9	121.9 (2)
C15—N2—C1	121.7 (2)	C10—C9—C8	118.2 (2)
C3—N2—C1	117.0 (2)	C10—C9—C1	122.6 (2)
N2—C1—C9	111.8 (2)	C8—C9—C1	118.8 (2)
N2—C1—C12	110.1 (2)	C9—C10—C5	119.7 (2)
C9—C1—C12	106.0 (2)	C9—C10—C4	119.3 (2)
N2—C1—C11	109.2 (2)	C5—C10—C4	120.9 (2)
C9—C1—C11	111.5 (2)	O1—C11—C1	110.0 (2)
C12—C1—C11	108.2 (2)	O2—C13—O1	122.8 (2)
N2—C3—C4	109.9 (2)	O2—C13—C14	124.7 (2)
C10—C4—C3	108.8 (2)	O1—C13—C14	112.6 (2)
C6—C5—C10	121.3 (2)	O3—C15—N2	122.0 (2)
O4—C6—C5	125.4 (2)	O3—C15—C16	119.1 (2)
O4—C6—C7	115.2 (2)	N2—C15—C16	119.0 (2)
C5—C6—C7	119.4 (2)		

Data collection: *Kuma KM-4 Software* (Kuma, 1991). Cell refinement: *Kuma KM-4 Software*. Data reduction: *Kuma KM-4 Software*. Program(s) used to solve structure: *SHELXS86*

(Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: CF1035). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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## 2-(2-Pyridyl)pyridinium Triiodide

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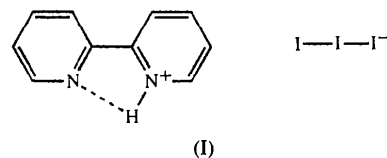
### Abstract

The title structure,  $C_{10}H_9N_2^+ \cdot I_3^-$ , consists of 2-(2-pyridyl)pyridinium cations and near-symmetric essentially linear triiodide anions [ $I—I = 2.902$  (1) and  $2.920$  (1) Å, and  $I—I—I = 177.88$  (5)°]. The cation has a *syn* configuration, with an intramolecular  $N—H \cdots N$  hydrogen bond:  $H—N2$  and  $H \cdots N1 = 1.13$  (11) and  $1.83$  (10) Å, respectively, and  $N2—H \cdots N1 = 124$  (8)°. The two heterocyclic rings are not coplanar, the angle between the rings being  $9.6$  (8)°.

### Comment

The title compound, (I), was obtained from a reaction scheme which involved the sequential addition to 4,5-dibenzoylthio-1,3-dithiole-2-thione in MeOH of NaOMe, 2,2'-bipyridyl and  $SnI_4$ , and after a work-up

which involved acidification and fractional crystallization from MeOH. The X-ray crystallography was carried out to identify the unexpected product unambiguously.



The title compound exists as an ionic species, with discrete cations and anions. The heterocyclic rings in the 2-(2-pyridyl)pyridinium cation have a *syn* arrangement (Fig. 1), with an angle of  $9.6$  (8)° between the perpendiculars of the planes of the two rings. The acidic H atom, bonded to N2, is intramolecularly hydrogen bonded to N1, with bond lengths for  $H—N2$  and  $H—N1$  of  $1.13$  (11) and  $1.83$  (10) Å, respectively, and an  $N2—H \cdots N1$  angle of  $124$  (8)°. The intramolecular  $N1 \cdots N2$  separation is  $2.64$  (2) Å.

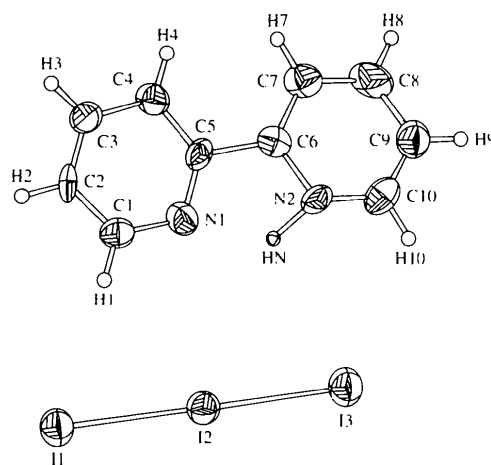


Fig. 1. The asymmetric unit of  $C_{10}H_9N_2^+ \cdot I_3^-$  showing the atom-numbering scheme. Displacement ellipsoids of non-H atoms are at the 40% probability level and H atoms are shown as spheres of arbitrary radii.

There are a number of (2-pyridyl)pyridinium compounds listed in the Cambridge Structural Database (Allen & Kennard, 1993). (2-Pyridyl)pyridinium cations have generally been shown to have *syn* structures in ionic complexes, with intramolecular  $N—H \cdots N$  hydrogen bonds, and with small angles between the planes of the two aromatic rings (see, for example, Figgis, Skelton & White, 1978; Khan, Kumar & Tuck, 1984; Chantler & Maslen, 1989; Decurtins, Schmale, Schneuwly & Oswald, 1993).

The triiodide anion is almost linear [ $I3—I2—I1 = 177.88$  (5)°] and almost symmetrical, with  $I—I$  bond lengths of  $2.920$  (1) ( $I2—I1$ ) and  $2.902$  (1) Å ( $I2—I3$ ).