$C_{21}H_{43}N_5O_8 \cdot 2.5H_2SO_4 \cdot 2H_2O$: C, 32.55; H, 6.76; N, 9.04; S, 10.35. Found: C, 32.5; H, 6.9; N, 9.4; S, 9.8. 2-Hydroxygentamicin C_2 (**3b**): mp 115–119 °C; ^1H NMR (D_2O) δ 5.82, 5.56 (anomeric H, 2 H) 5.20 (exchangeable H, 13 H) 3.09 (NCH_3, 3 H) 3.0–4.6 (CHO, CHN, CH_2O, 13 H) 1.9–2.5 (CH_2CH_2, 4 H) 1.73 ppm (CH_3C, CH_3CH, 6 H); MS (MH^+) 480 fragments *m/e* 436, 366, 362, 349, 338, 321, 320, 160, 143;[13] $[\alpha]^{25}{}_D$ +137.1 (0.2% H_2O) Anal. Calcd for $C_{20}H_{41}N_5O_8 \cdot 2.5H_2SO_4 \cdot 3H_2O$: C, 30.85; H, 6.73; N, 8.99; S, 10.29. Found: C, 30.5; H, 6.5; N, 9.0; S, 10.1.

The C_1 component, **3a**, from both experiments was combined in a 2:1 mixture and the ^{13}C NMR spectrum was obtained with one set of 21 lines present indicating that both experiments gave the same compound. The values obtained for the chemical shifts were consistent with streptamine (**B**) as the central ring with purpurosamine (C) and garosamine (A) carbon shifts corresponding very well to the values reported by Morton et al.[14,15] for gentamicin antibiotics. The ^{13}C NMR comparisons of the C_2 (**3b**) component from both sources could not be accomplished to our satisfaction because of different impurities present in the two samples.

Rinehart et al.[16] have suggested a deoxyinosose (Scheme I, X = H) as an intermediate in the biosynthetic pathway to deoxystreptamine (**1**), instead of the earlier proposed cyclization of a 2,6-diamino-5-oxohexose.[17] In view of our present result with inosose **5**, it became of interest to prepare 2,4/3,5-tetrahydroxycyclohexanone (**6**, *deoxyscyllo-ms*-inosose). We prepared *dl*-viboquercitol (**8**) from *myo* inositol (**7**) by the method of McCasland and Horswill[18] and carried out the microbiological oxidation of **8** to *dl*-2,4/3,5-tetrahydroxycyclohexanone (**6**) using *Acetobacter suboxydans*,[19] a procedure used by Posternak for the oxidation of the individual enantiomers.

Theoretically one enantiomer of **6** (structures **6** and **8** depicted in Scheme I should not imply absolute configuration) should be converted by the mutant of *M. purpurea* to deoxystreptamine. In fact, when **6** is supplemented to a growing culture of our mutant, the gentamicin C complex (**2**) of antibiotics is produced. The components on TLC (silica gel Brinkmann 60 F254 lower phase of a $CHCl_3$:MeOH:concentrated NH_3; 1:1:1 system) are identical with the authentic gentamicin C complex (**2**). The molecular ions (M^+) and mass fragments (*m/e*) of the isolated components were identical with authentic gentamicin C_1 (**2a**), C_2 (**2b**), and C_{1a} (**2c**).

The incorporation by *M. purpurea* deoxystreptamine-negative mutant of 2,4/3,5-tetrahydroxycyclohexanone (**6**) is supportive of the suggested biosynthetic pathway of deoxystreptamine (**1**) by Rinehart et al.[15]

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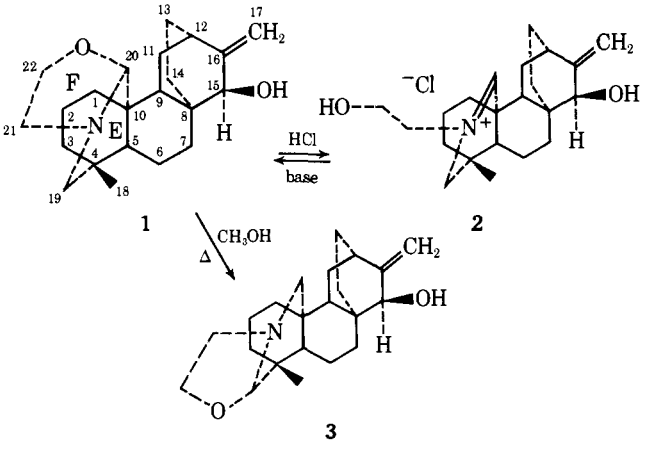
The Conformational Analysis of the E and F Rings of Atisine, Veatchine, and Related Alkaloids. The Existence of C-20 Epimers

Sir:

Atisine, the major alkaloid of *Aconitum heterophyllum*, has been the subject of extensive chemical study because of its interesting chemical features and complex structure (**1**). The latter was established by the work of several investigators[1-6] and was confirmed by two elegant total syntheses.[7,8] Atisine is an amorphous strong base (pK_a 12.8) that undergoes a facile isomerization of the oxazolidine ring to isoatisine (**3**) (pK_a 10.3) by treatment with methanolic alkali[9] or even by simple refluxing in methanol.[10]



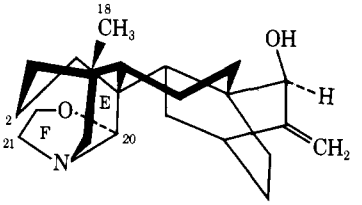
In 1968 we postulated on the basis of a ^1H NMR study that atisine exists as two different conformers, **4A** and **4B**, in 1:2 ratio, respectively, in $CDCl_3$ solution at room temperature.[11] We suggested that the two C-4 methyl singlets in the ^1H NMR spectrum of atisine are due to the two possible conformations of ring E. Conformation **4A** in which ring E is in a chair form would account for the smaller upfield signal of the C-4 methyl group and conformation **4B**, in which ring E is in a boat form, would account for the larger signal of the C-4 methyl group at lower field. This interpretation seemed to be supported by a temperature dependence study of the C-4 methyl signals of

Table I. Carbon-13 Chemical Shifts and Assignments for Atisine **1**, Isoatisine **3**, Atisinone **5**, Veatchine **6**, and Garryine **7**[a]

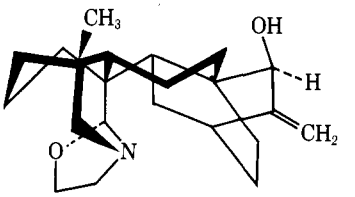
Carbon	1A	1B	3	5A	5B	6A	6B	7
1	42.0[b]	42.0[b]	40.6[b]	40.8[b]	40.8[b]	41.7	41.3	40.6
2	22.4	21.7	22.1	22.4	21.5	18.6	19.2	20.6
3	41.0[b]	40.9[b]	40.0[b]	40.5[b]	40.5[b]	37.1	37.1	40.6
4	33.8	28.2	38.1	33.8	27.7	34.1	34.1	40.3
5	51.6	48.9	48.6	51.5	48.6	52.8	52.3	50.6
6	17.8	18.5	19.2	17.4	18.2	18.6	17.4	18.2
7	34.6	32.0	31.9	34.2	34.2	33.9	33.9	33.8
8	37.5	37.5	37.5	44.7	44.7	47.3	47.5	47.4
9	40.0	39.6	39.6	44.2	44.2	51.6	51.1	49.1
10	40.4	40.4	35.9	41.7	41.7	40.6	40.3	35.9
11	28.2	28.2	28.1	29.6	29.6	22.7	21.8	22.3
12	36.6	36.6	36.4	36.2	36.2	31.2	30.3	32.4
13	27.7	27.7	27.6	27.7	27.7	42.4	42.4	41.7
14	25.5	25.5	26.4	29.3	29.3	35.1	35.1	36.8
15	77.0	77.0	76.8	204.0	203.0	82.8	84.3	82.7
16	157.5	157.5	156.2	147.4	147.1	160.7	161.2	159.6
17	108.9	108.4	109.6	116.3	115.9	107.4	107.8	108.5
18	26.7	26.1	24.3	26.6	25.9	25.9	26.4	24.4
19	56.4	53.3	98.4	55.9	53.2	56.4	55.9	98.2
20	93.9	94.2	49.8	93.4	93.4	92.6	93.3	51.1
21	50.3	50.3	54.9	50.1	50.1	50.2	49.8	54.8
22	64.1	59.2	58.6	64.3	59.2	64.3	58.8	58.7

[a] Carbon-13 spectra were taken at 25.03 MHz in the Fourier mode using a JEOL-PET-100 spectrometer in conjunction with a EC-100-20K memory computer. Samples were dissolved in $CDCl_3$ containing Me_4Si as an internal standard. Concentrations were about 0.8–1.0 M. All assignments are based on off-resonance decoupling spectra. [b] These assignments may be interchanged.

atisine. The two C-4 methyl signals coalesced to a single resonance line of three proton area at approximately 85 °C. Subsequently, on the basis of a deuterium study, it was suggested that atisine in solution is a mixture of isomers which differ in configuration at C-20 and which are interconvertable via a zwitterion.[12]

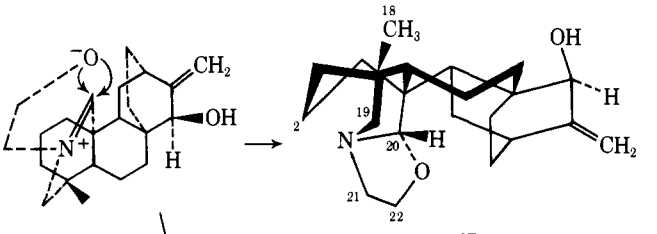


4A

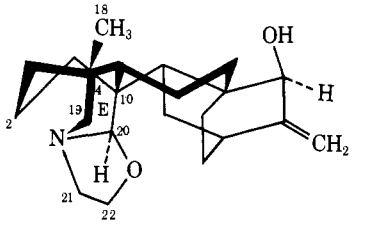


4B

To settle the question of whether atisine is a mixture of conformers **4A** and **4B** or a mixture of C-20 epimers, we examined the carbon-13 NMR spectra of atisine and a group of related alkaloids (Table I). Assignment of the resonances to individual carbon atoms in atisine (**1**), isoatisine (**3**), atisinone (**5**), veatchine (**6**), and garryine (**7**) was achieved by using off-resonance decoupling techniques, chemical-shift theory, direct analysis of nonprotonated carbon centers, and comparison with other related alkaloids[13] (e.g., dihydroatisine, atidine, etc). The carbon-13 NMR spectrum of atisine in $CDCl_3$ at room temperature shows two different sets of signals for the oxazolidine ring (ring F), the piperidine ring (ring E), and the C-4 methyl group. Because rings A and B in the atisine skeleton are held in a rigid conformation, the only conformationally mobile moieties that can give the two sets of signals are the E and F rings. But considering the free energy difference between conformers **4A** and **4B**, two different sets of signals for these two conformers at room temperature are not likely.[14] The equilibrium between conformers **4A** and **4B** at room temperature would be so fast in solution that only one set of signals should appear in the ^1H and ^{13}C NMR spectra. Thus, the data do not indicate the existence of two conformers **4A** and **4B**.



1B



1A

The presence of two sets of signals for the E and F rings in the ^{13}C NMR spectrum of atisine suggests the existence of a mixture of epimers. The fact that the oxazolidine ring of atisine is regenerated from atisinium chloride (**2**), in which C-20 is trigonal, by treatment with strong base suggests that formation of the oxazolidine ring takes place from both sides of the trigonal C-20 carbon to give two epimers. These two C-20 epimers of atisine are represented by structures **1A** and **1B** which are consistent with the ^{13}C NMR spectrum of atisine.

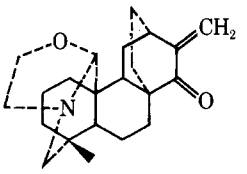
To demonstrate further the existence of the C-20 epimers in atisine a temperature dependence study of atisine in deuterated toluene was performed (Table II). The carbon-13 NMR data indicate that the isomerization of atisine (**1**) to

Table II. A Temperature Dependence Study of Atisine[a]

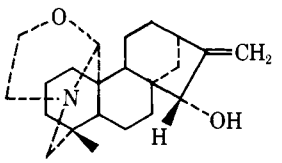
Temp, °C	Atisine 1A[b] %	Atisine 1B %	Isoatisine 2 %
25	65	35	—
40	65	35	—
56	55	35	10
70	55	35	10
90	50	30	20
RT[c]	50	30	20
RT[d]	50	30	20

[a] Study was performed in deuterated toluene (d_8) using HMDS[$(CH_3)_3Si]_2O$ as an internal reference. [b] The percentage of compounds in the mixture at a given temperature was determined by monitoring the C-20 peak for **1A** and **1B** and the C-19 peak for **2** in the ^{13}C NMR spectrum. [c] The ^{13}C spectrum was taken at room temperature after the sample had been held at 90 °C for 50 min [d] The spectrum was taken 60 h later at room temperature after temperature had been held at 90 °C for 50 min.

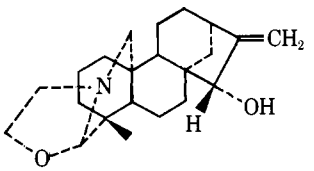
isoatisine (**3**) occurs as low as 56 °C but, that even at 90 °C, the two sets of signals do not coalesce to a single resonance. These results confirm the existence of the C-20 epimers of atisine. The ^{13}C NMR analysis also indicates that epimer **1A** exists in greater amount than **1B**, presumably, because in **1A** the formation of the oxazolidine ring occurs from the least hindered side of the C-20 carbon.



5 atisinone



6 veatchine



7 garryine

The carbon-13 NMR spectra of atisinone (**5**) and veatchine (**6**) also show two sets of signals for ring E and F carbons (Table I), a result which indicate that these compounds also exist as a mixture of C-20 epimers.

It should be noted that early work[15] on the configuration of atisine and related alkaloids assumed, without evidence, a β configuration for the hydrogen at C-20. Because atisine and veatchine are isolated as the ternary iminium salts (e.g., **2**) which on treatment with base generate the respective alkaloids, the question of which of the C-20 epimers of each alkaloid occurs in the plant is unanswered.

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A New Class of Highly Conductive Molecular Solids: the Partially Oxidized Phthalocyanines

Sir:

Crystals composed of molecular ions and exhibiting strongly anisotropic metallic behavior are currently of great experimental and theoretical interest.[1] These materials invariably consist of stacks of strongly interacting, planar inorganic (e.g., $Pt(CN)_4^{-m}$) or organic ($TCNQ^{-n}$) ions; weak interactions between the stacks lead to the anisotropic transport properties. It appears that high conductivity requires a nonintegral formal oxidation state for the ions within a stack,[1] a result which may be understood in terms of the low "conduction electron density" in a molecular crystal.[2] Since these materials are not common, a broadly applicable synthetic procedure would have considerable significance. In most instances, the plausible approach of a substoichiometric oxidation of planar organic molecules or transition ion complexes of integral oxidation state does not consistently produce the desired mixed valencies. However, we anticipated that iodine[3,4] would be an especially advantageous oxidant,[3] because of the high stability of I_3^- in nonpolar environments,[5] and because of the ability of I_3^- to accommodate itself to channels in one-dimensional lattices.[3,4] Thus, oxidation of a divalent metal complex according to eq 1 would yield a trivalent metal ion if I^- were produced, but a nonintegral oxidation state if all metal sites in the material were crystallographically similar and if only I_3^- were formed, e.g., $(LM)(I_3^-)_{1/3}$ where M has a formal oxidation state of 2.33. Furthermore, the products of such oxidations are particularly amenable to characterization by spectroscopic means. We confirm here the utility of this synthetic approach, and report that, when applied to the phthalocyanines, it results in an extensive new class of highly conducting molecular solids.

$$(L)M^{II} + \tfrac{1}{2}I_2 \rightarrow (LM)(I) \qquad (1)$$

The oxidation[6] of purified Fe, Co, Ni, Cu, Zn, Pt, and metal-free phthalocyanines, by iodine vapor or solutions (e.g., chlorobenzene), results in darkly colored solids with a range of stoichiometries[6,7a] (eq 2), the exact composition obtained depending on the conditions. The reaction is reversible, and iodine can be completely removed by warming the solids in vacuo.[7b] That these materials exhibit truly mixed valency is supported by several lines of evidence. First, resonance Raman spectroscopy shows that the iodine is present as I_3^- in all samples with $x < 3$. The Raman spectra taken with spinning samples and 6471, 5145, or 4880 Å excitation clearly reveal the resonance-enhanced totally symmetric I–I–I$^-$ stretch (ν 105–108 cm^{-1})[3b,8] and expected overtone progression[3b,8] of I_3^- (Figure 1). Calculated anharmonicity constants and