Table I. Vibration Frequencies (cm^{-1}) in Substituted Palladium(II) Thiocyanate Complexes[a]

Complex	C–N str	C–S str	–SCN bend	Pd–S str
Sulfur bonded				
$[Pd(Ph_3As)_2(SCN)_2]$	2120[b]	*d*	418[b]	311
$[Pd(bipy)(SCN)_2]$	2117[c]	700[c]	*d*	319
$[Pd(Et_4dien)(SCN)]SCN$	2103	710[e]	435	295
$[Pd(py)_2(SCN)_2]$	2112[b]	*d*	424[b]	305
$[Pd(Ph_3Sb)_2(SCN)_2]$	2119[c]	*d*	440	290
$[Pd(phen)(SCN)_2]$	2116[b]	697[b]	418[b]	305
Nitrogen bonded				
$[Pd(Ph_3As)_2(NCS)_2]$	2085[b]	854[b]	*d*	265
$[Pd(bipy)(NCS)_2]$	2100[b]	845[b]	458[b]	261
$[Pd(Et_4dien)(NCS)]SCN$	2080	832[e]	472	268
$[Pd(Ph_3P)_2(NCS)_2]$	2095[b]	853[b]	*d*	270
$[Pd(n\text{-}Bu_3P)_2(NCS)_2]$	2100[b]	846[b]	448[b]	*d*

[a] Abbreviations: Ph, phenyl; bipy, 2,2′-bipyridine; py, pyridine; phen, 1,10-phenanthroline; *n*-Bu, *n*-butyl; Et_4dien, 1,1,7,7-tetraethyldiethylenetriamine. [b] Frequencies taken from ref 1. [c] Frequencies taken from ref 8. [d] Band masked by absorption due to the organic ligands. [e] Frequencies taken from ref 11.

The Pd–N and Pd–S stretching frequencies should occur in still a fourth (lower frequency) region of the infrared spectrum, and we have accordingly investigated several palladium(II) complexes in this region. Forster and Goodgame[9] and Sabatini and Bertini[7] have reported stretching frequencies for various transition metal thiocyanate complexes and found values in the neighborhood of 300 cm^{-1} for Pd–SCN complexes. Kharitonov, Tsintsadze, and Porai-Koshits[10] have calculated that peaks due to Pd–NCS stretching should be about 45 cm^{-1} lower than those for Pd–SCN, if the M–N and M–S force constants are approximately the same.

Three pairs of palladium(II) thiocyanate linkage isomers, recently prepared by Burmeister and Basolo[8] and Baddley and Basolo,[11] seemed especially appropriate for use in arriving at assignments for the Pd–ligand atom vibration frequencies. The sulfur-bonded forms of these linkage isomers (*i.e.*, $[Pd(Ph_3As)_2(SCN)_2]$ and $[Pd(Ph_3As)_2(NCS)_2]$, $[Pd(bipy)(SCN)_2]$ and $[Pd(bipy)(NCS)_2]$, $[Pd(Et_4dien)(SCN)]SCN$ and $[Pd(Et_4dien)(NCS)]SCN$) are prepared from $K_2[Pd(SCN)_4]$ by the replacement of two or three thiocyanate groups by other ligands. Inasmuch as this starting compound possesses Pd–S bonds,[7] the complexes as initially obtained also have this structure. Each of these S-bonded compounds is converted to the N-bonded isomer on standing or with increase of temperature. Each pair of these linkage isomeric compounds thus provides a unique opportunity to examine the Pd–S and Pd–N stretching frequencies in the presence of identical ligand atmospheres. Spectra of these complexes as well as those of several other Pd–NCS and Pd–SCN compounds were obtained and assignments made in all cases by comparison with the spectra of the analogous chloro complexes. The results are given in Table I.

The results agree with the two previously reported Pd–SCN stretching frequencies of 298 and 300 cm^{-1} for $((CH_3)_4N)_2[Pd(SCN)_4]$[9] and $K_2[Pd(SCN)_4]$,[7] respectively, confirm the calculations of Kharitonov and coworkers,[10] and indicate that the M–N and M–S force constants are about the same. There appears to be a definite correlation of absorption peak positions in the region 320–260 cm^{-1} with sulfur- or nitrogen-bonded complexes. All substituted Pd–SCN complexes exhibit a peak in the region 320–290 cm^{-1}, and all Pd–NCS complexes a peak in the region 270–260 cm^{-1}.

Perhaps a word of caution is in order for anyone considering using the far-infrared method on these or similar compounds. Spectra of a number of these complexes were obtained by both the CsI pellet and Nujol mull techniques. In every case which involved the pellet technique, exchange of thiocyanate ligands by iodide from the CsI matrix appeared to have taken place.

The complexes were prepared by the procedures of Burmeister and Basolo[8] and Baddley and Basolo.[11] Infrared spectra (700–200 cm^{-1}) were obtained by F. S. Bonomo of the Denver Research Institute and recorded on a Beckman Model IR-7 spectrophotometer using Nujol mulls on polyethylene plates. Spectra in the sodium chloride region were obtained on a Beckman Model IR-8 spectrophotometer using Nujol mulls. The sulfur-bonded forms of the linkage isomers were stored in Dry Ice up to the time their spectra were obtained.

R. N. Keller, N. B. Johnson, L. L. Westmoreland
Department of Chemistry, University of Colorado
Boulder, Colorado 80302
Received February 26, 1968

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The Stereochemistry of Jervine and Related Alkaloids[1, 2]

Sir:

Evidence is advanced herewith for revision of the configuration at C-17 in the formulation of jervine (I).[3,4] The argument also provides a firm basis for assignment of complete relative and absolute configurations to jervine (I), veratrobasine (II), 11-deoxojervine (III), veratramine (IV), and verarine (V).[5]

A recent X-ray diffraction study of veratrobasine revealed that the alkaloid possesses the structure and *relative* configuration II.[6] Although the structural resemblance to jervine was noted, the authors commented: "It remains to be shown whether the stereochemistry of the two molecules is identical at corresponding asymmetric centers." The similarity of the physical properties of veratrobasine[7] to those reported for jervin-11β-ol[8] suggested the possible identity of the two materials. The hypothesis was tested by direct

(1) Veratrum Alkaloids. LIV.
(2) This investigation was supported by Public Health Service Research Grant No. HE-02275 from the National Heart Institute.
(3) The 17α-oxide and 20α-methyl configurations for jervine were originally suggested solely on the basis of biogenetic analogy to normal steroids; see, *e.g.*, O. Wintersteiner, *et al.*, *J. Am. Chem. Soc.*, **76**, 5609 (1954); **78**, 6193 (1956).
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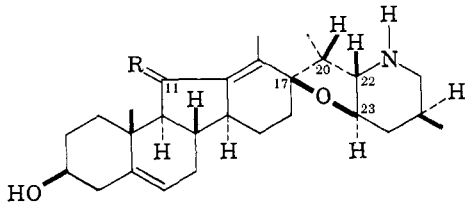
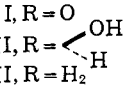
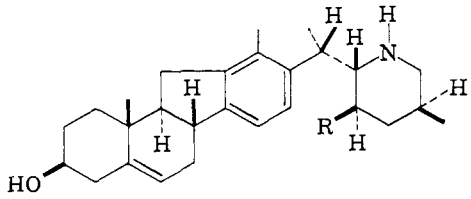


I, R = O
II, R = 
III, R = H_2



IV, R = OH
V, R = H

comparison of a sample of jervin-11β-ol, prepared by reduction of jervine,[8] with an authentic sample of veratrobasine[9] (by mixture melting point, mixture tlc, optical rotation, high-resolution ir, nmr, and mass spectral comparisons[10]); the respective materials were, indeed, found to be identical.

The interrelation of veratrobasine (II) with jervine (I) establishes: (1) the β orientation of the 17-oxide in jervine (and, hence, in 11-deoxojervine (III)[11]); (2) the α orientation of the 20-methyl group in jervine (and, hence, in 11-deoxojervine (III),[11] veratramine (IV),[12] and verarine (V)[13]), as suggested earlier by biogenetic analogy;[3] (3) the C-22α and C-23β configurations for the substituents at the respective positions in jervine and related alkaloids, in confirmation of the recently revised assignments on the basis of elegant chemical studies by Johnson, *et al.*;[14] and (4) the absolute configuration of veratrobasine (II) as that which occurs in normal steroids, for the absolute confirmation of jervine (I) has been established earlier by interrelation with hecogenin.[15,16]

(9) We thank Dr. D. Stauffacher, Sandoz Ltd., Basel, for the authentic sample of veratrobasine.

(10) We thank Dr. G. Van Lear and Dr. F. W. McLafferty of the Purdue Mass Spectrometry Center, supported under U. S. Public Health Service Grant FR-00354, for the mass spectral data.

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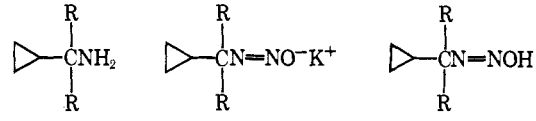
S. Morris Kupchan, Matthew I. Suffness[17]
Department of Pharmaceutical Chemistry
University of Wisconsin, Madison, Wisconsin 53706
Received April 2, 1968

Fate of the Cyclopropylcarbinyl Cation in Aqueous Base[1,2]

Sir:

Recently we contrasted nitrous acid deamination of 2-aminooctane with hydrolysis of octane-2-diazotate and showed that free carbonium ions were largely bypassed in the latter process.[3] Some years ago, discussing the methylene group scrambling observed in the deamination of cyclopropylcarbinylamine (I), Roberts remarked: "Matters would be greatly helped by study of these interconversion reactions in bonafide carbonium processes in much more nucleophilic solvents so that the intermediates . . . could be trapped before they become so extensively interconverted."[4] Therefore, we extended our studies[3] to a comparison of the nitrous acid deamination of I (pH 2) and the hydrolysis of the related diazotate, II (pH 14).[2] In both cases, the products included cyclopropylcarbinol, cyclobutanol, and allylcarbinol. Over several experiments,[2] typical values for the ratio of cyclopropylcarbinol to cyclobutanol ("product ratio") were 1.16 for the deamination of I



I, R = H; I-*d*, R = D
II, R = H; II-*d*, R = D
III, R = H; III-*d*, R = D

and 1.28 for the hydrolysis of II, suggesting that SN2 displacement on the diazotic acid III was not the major pathway to cyclopropylcarbinol at high [OH^-] and that "the diazotate hydrolysis occurs *via* cationic intermediates *similar* to those involved . . . in the deamination of cyclopropylcarbinylamine."[2] We now report a closer examination of these reactions.

II was hydrolyzed with water containing 22.6% ^{18}O. The product alcohols were isolated by vpc, converted to benzoates with benzoyl chloride–pyridine, and analyzed by mass spectroscopy. The cyclopropylmethyl benzoate contained 19.9% ^{18}O and the cyclobutyl benzoate contained 19.3% ^{18}O, indicating that the alcohols had been formed with *ca.* 11.9 and 14.7% return (respectively) of the ^{16}OH originally present in the diazotic acid III derived from II.[5] A parallel experiment with the deuterated diazotate, II-*d*, afforded cyclopropylmethyl benzoate containing 19.7% ^{18}O, corresponding to 12.9% ^{16}OH return.

These experiments should be compared to the hydrolysis of octane-2-diazotate in $H_2{}^{18}O$ in which 2-octanol is formed with 40% return of the diazotate's ^{16}OH.[3] Assuming the main course of diazotate hydrolysis to be that outlined in eq 1, the observed greater

$$\underset{\text{III}}{RN{=}NOH} \longrightarrow [R\cdots\overset{\delta+}{N}{=}N\cdots\overset{\delta-}{O}H] \longrightarrow \underset{\text{IV}}{[R^+OH^-]} \longrightarrow ROH \qquad (1)$$

loss of original hydroxide from III could be attributed to a greater stability and hence longer lifetime of the cyclopropylcarbinyl cation *vis-à-vis* the 2-octyl cation, leading to more complete hydroxide exchange with solvent water at the ion-pair stage, IV.[6]

(1) The Solvolysis of Alkyl Diazotates. IV.

(2) Part III: R. A. Moss and F. C. Shulman, *Tetrahedron*, **24**, 2881 (1968).

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(5) Dilution of the ^{18}O pool by ^{16}O from II was negligible.

(6) (a) The possibility that ^{18}O incorporation occurs at a prior stage, *via* an equilibrium such as a, must be considered. Although hydrox-

$$RN{=}NOH \rightleftharpoons RN{\equiv}N^+\,OH^- \qquad (a)$$

ide exchange from a diazonium hydroxide ion pair would be likely if R was an *ordinary primary* alkyl group, it is unlikely in the present case where R is cyclopropylcarbinyl. Thus Whiting[6b] has shown that nitrogen loss from RN=NX involves essentially *synchronous* cleavage of