Infrared Spectra of Nicotine and Some of Its Derivatives

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Ultraviolet spectrophotometry has been used for the identification and characterization of tobacco alkaloids and related substances, but the ultraviolet spectra cannot be used to distinguish among alkaloids having equivalent degrees of conjugated unsaturation. Infrared spectra are presented in this paper for nicotine and five related alkaloids. These spectra are quite different for compounds having identical ultraviolet curves. Rapid and unambiguous identification of any one of these alkaloids is possible by comparison of the spectrum of an unknown with these infrared curves. The absence of an N—H stretching vibration in the spectrum of myosmine suggests that the accepted structure of this alkaloid is incorrect.

Table I. Infrared Bands Common to All Six Alkaloids, with Pyridine Bands for Comparison

Wave No., K.

Dihydro-meta-nicotine	Meta-nicotine	My-osmine	Nico-tine	Nico-tyrine	Nor-nicotine	Pyri-dine (*2*)
713	707	707	715	713	714	703
1025	1023	1025	1025	1021	1026	1030
1127	1123	1118	1117	1131	1125	..
1186	1184	1193	1191	1188	1190	..
1420	1416	1414	1418	1416	1427	..
1476	1474	1473	1478	1486	1479	1482
1572	1569	1567	1577	1568	1577	1572
sh	1585	1591	1592	1590	1592	1583
1916	1905	1915	1912	1930	1914	1923
2960	2939	2967	2970	2990	2970	2960

NICOTINE, nornicotine, and some of the myosmines and nicotyrines derived from them as dehydrogenation products have been prepared at this laboratory in a state of high purity. Their ultraviolet spectra were presented and discussed in earlier papers (*3, 9*). The infrared spectra of six of these alkaloids are presented in this paper. Although the ultraviolet spectra were not capable of distinguishing among the various alkaloids possessing equivalent degrees of conjugated unsaturation, the infrared spectra are distinctive and allow unambiguous identification of any one of these alkaloids. In particular, nicotine and nornicotine, whose ultraviolet spectra are essentially identical, show pronounced differences in the infrared, the most prominent being the stretching band at 3294 kaysers (*1*).

In general, those alkaloids having nitrogen-hydrogen groups show this pronounced band near 3300 K., while the band is absent in the tertiary-nitrogen alkaloids. One seeming exception is myosmine, which shows no band in the 3300 K. region, even in the solid state as a mineral-oil mull. This raises the question once more of the structure of myosmine. Although the accepted formula is I, it has been suggested (*7, 8*) that there may be tautomeric equilibrium with structure II. Some of the chem-

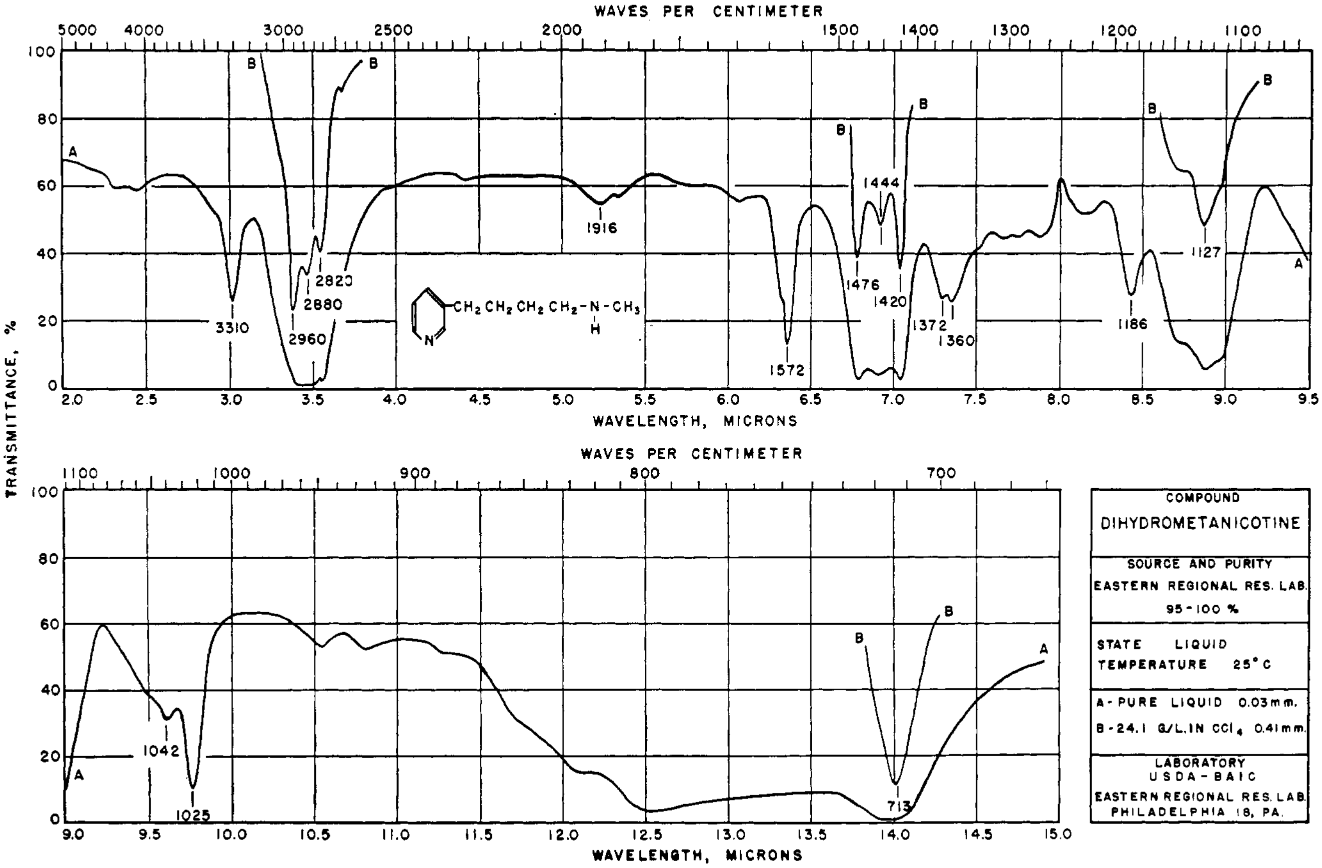
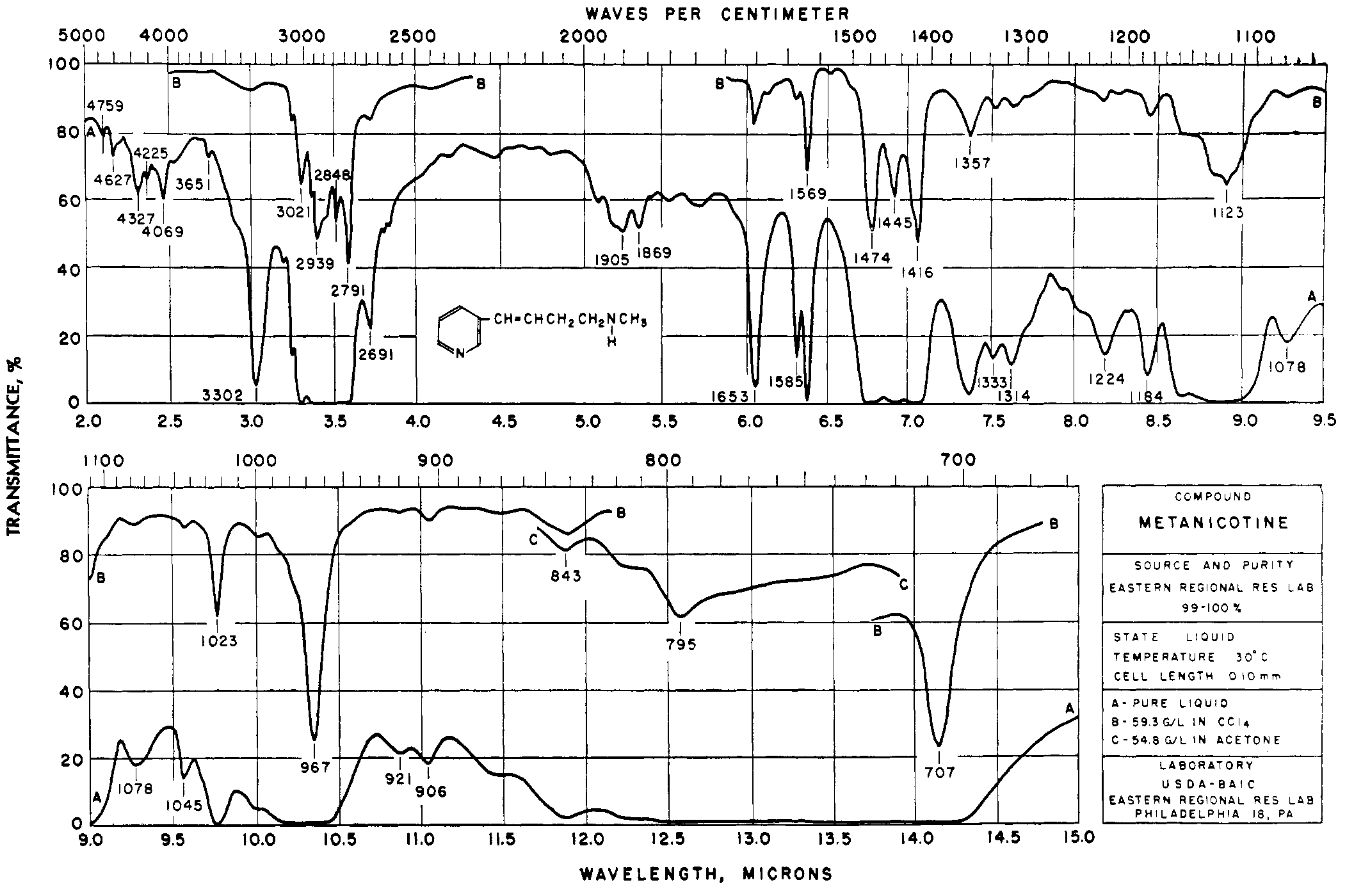
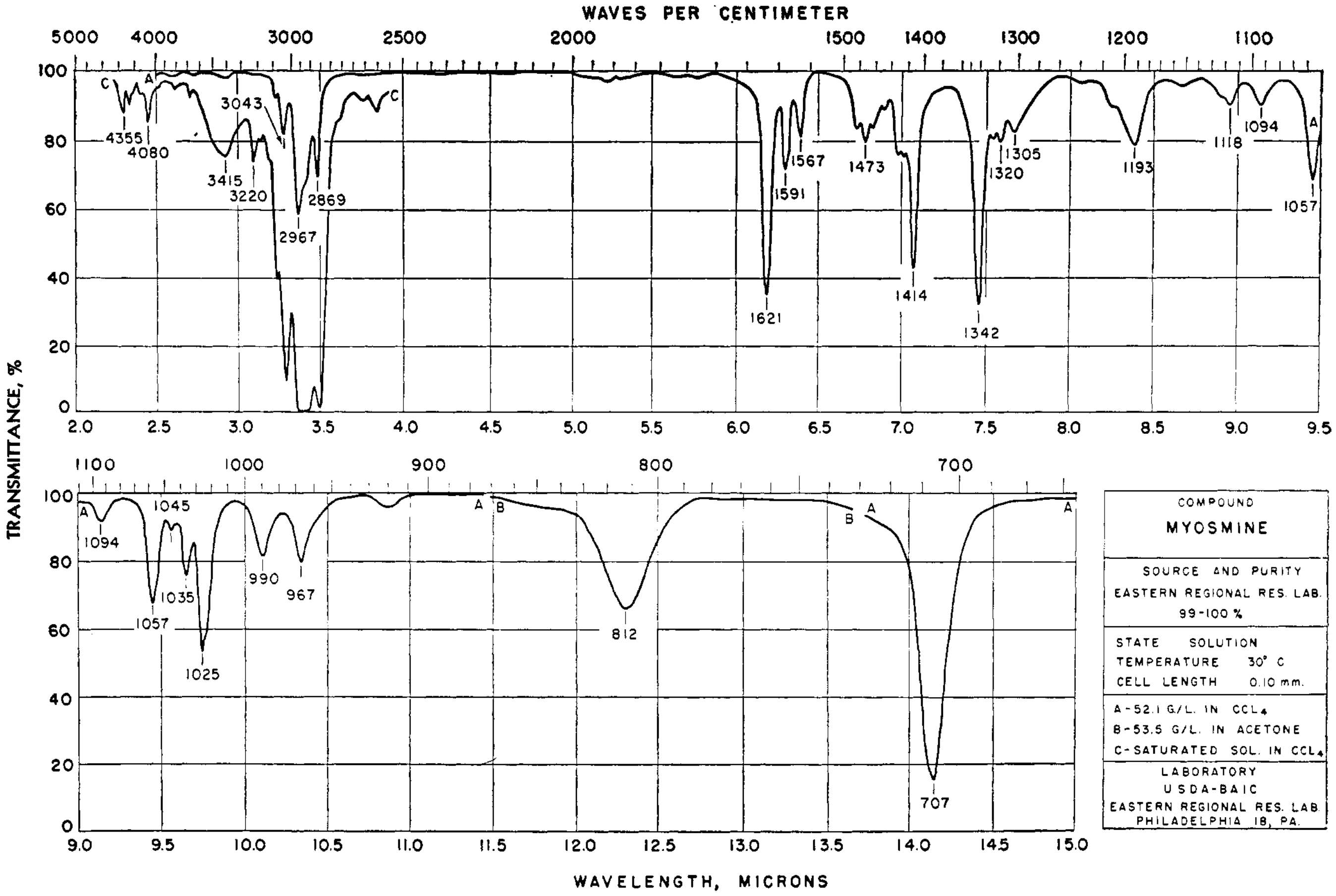


Figure 1. Infrared Spectrum of Dihydrometanicotine



COMPOUND
METANICOTINE
SOURCE AND PURITY
EASTERN REGIONAL RES LAB
99-100 %
STATE LIQUID
TEMPERATURE 30°C
CELL LENGTH 0.10 mm
A - PURE LIQUID
B - 59.3 G/L IN CCl_4
C - 54.8 G/L IN ACETONE
LABORATORY
USDA-BAIC
EASTERN REGIONAL RES LAB
PHILADELPHIA 18, PA

Figure 2. Infrared Spectrum of Metanicotine



COMPOUND
MYOSMINE
SOURCE AND PURITY
EASTERN REGIONAL RES. LAB.
99-100 %
STATE SOLUTION
TEMPERATURE 30° C
CELL LENGTH 0.10 mm.
A - 52.1 G/L. IN CCL_4
B - 53.5 G/L. IN ACETONE
C - SATURATED SOL. IN CCL_4
LABORATORY
USDA-BAIC
EASTERN REGIONAL RES. LAB
PHILADELPHIA 18, PA.

Figure 3. Infrared Spectrum of Myosmine

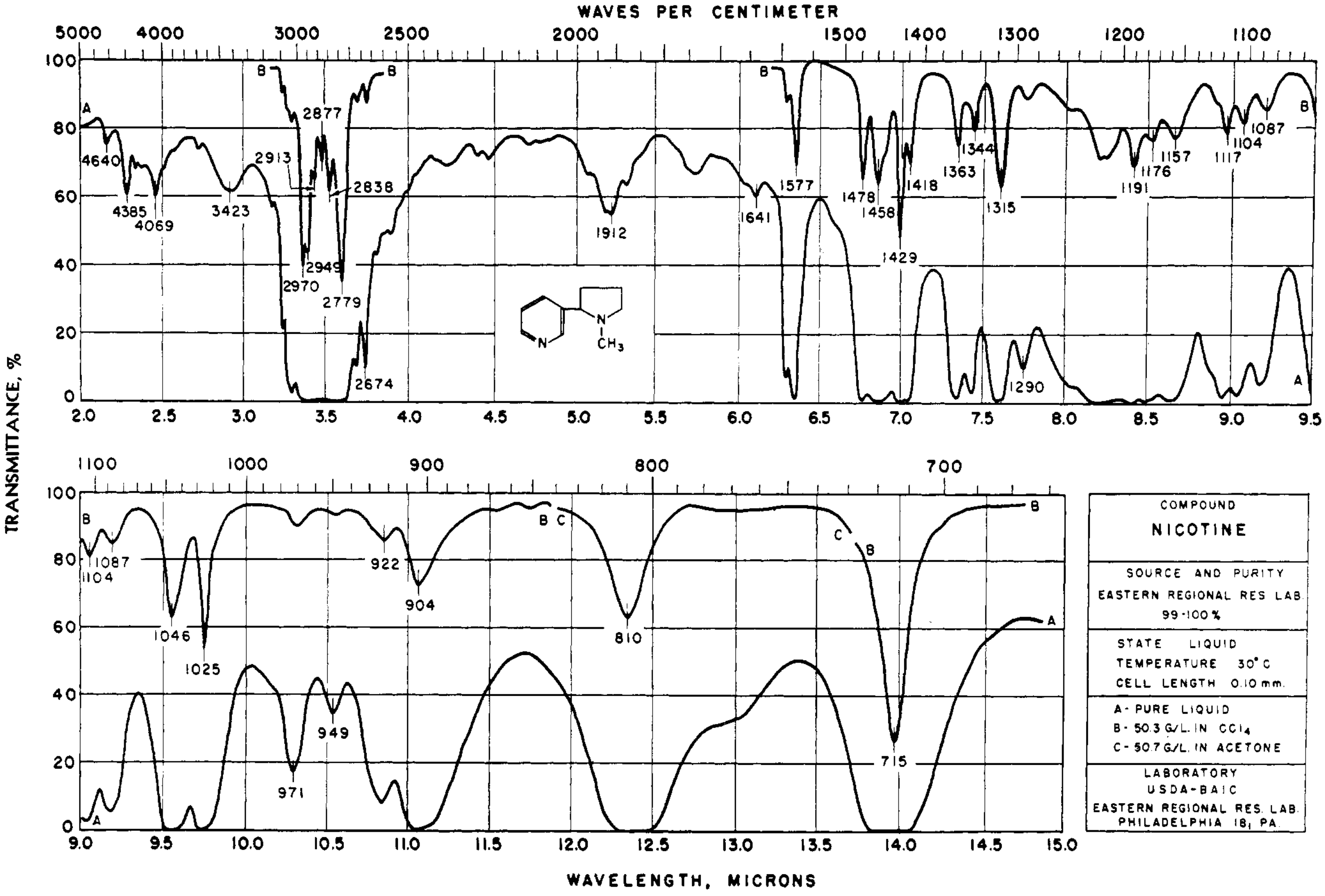


Figure 4. Infrared Spectrum of Nicotine

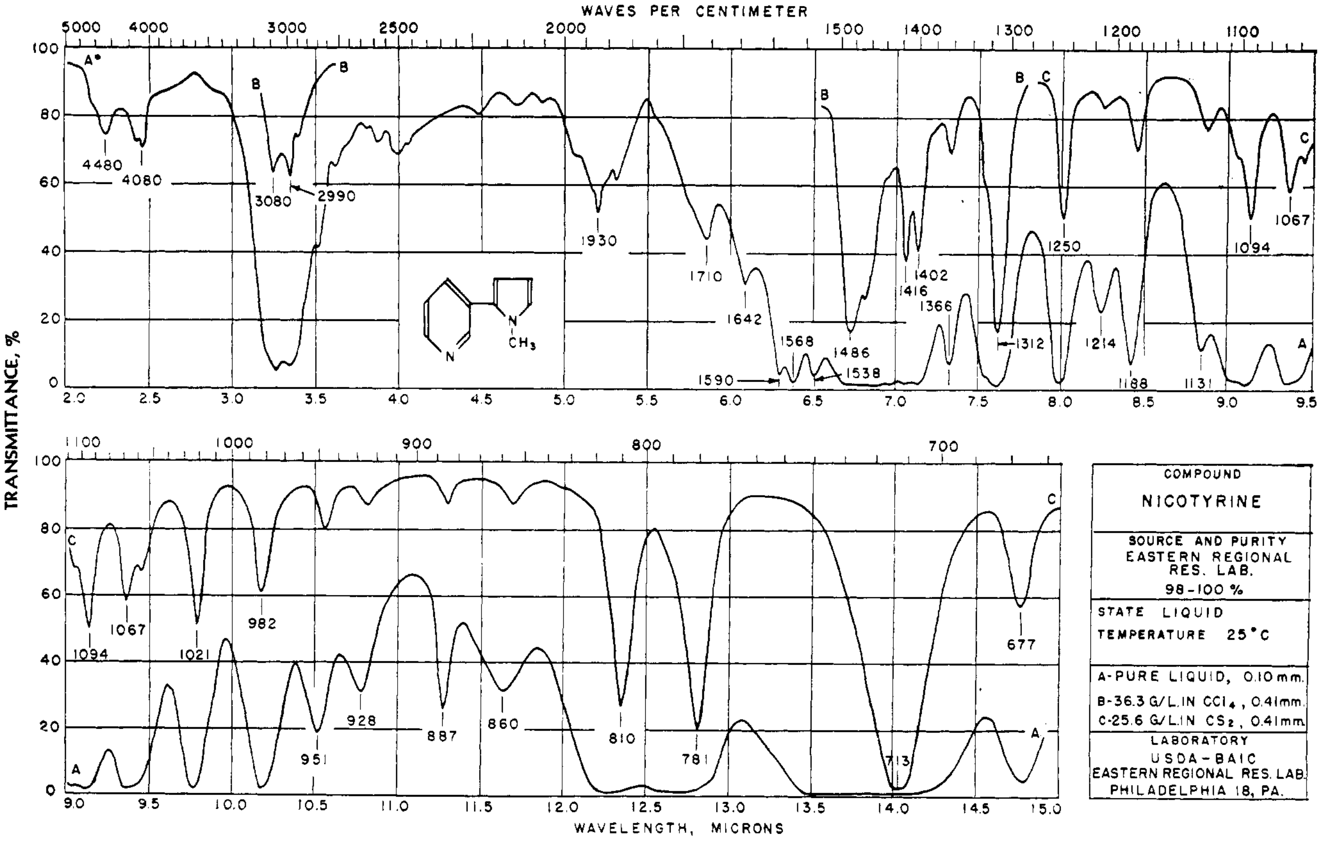


Figure 5. Infrared Spectrum of Nicotyrine

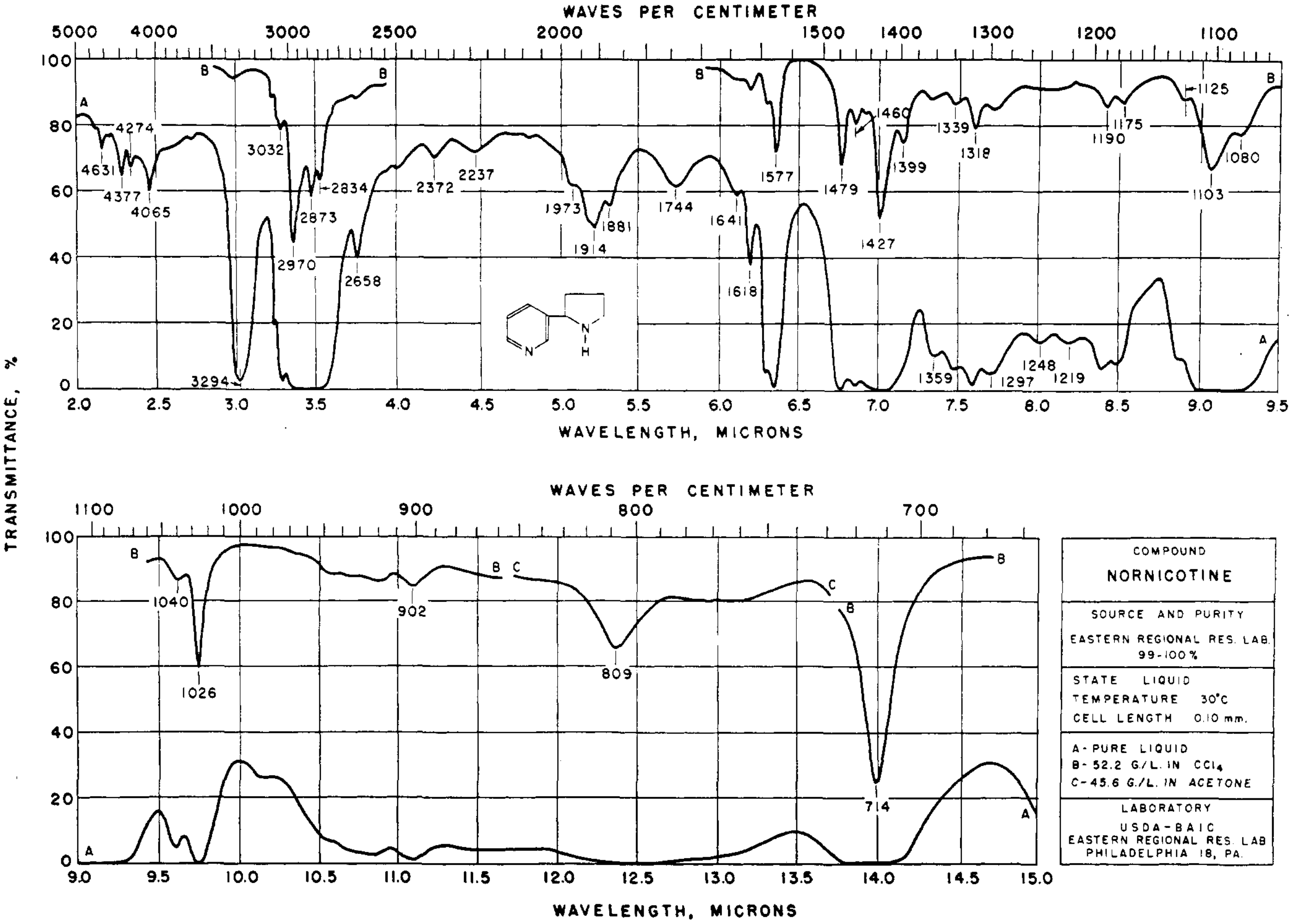
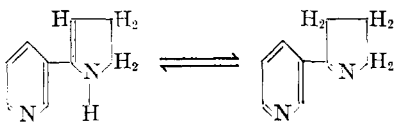


Figure 6. Infrared Spectrum of Nornicotine

ical reactions of myosmine (*4*) can also be interpreted in terms of II. Absence of a nitrogen-hydrogen band in the infrared suggests that the predominant tautomer in the equilibrium is II rather than the accepted structure. Witkop (*11*) has also called attention to the 1621 K. band as a possible C=N vibration in the 5-membered ring. Its much greater strength in myosmine than similar bands in metanicotine and nicotyrine suggests a C=N rather than a C=C linkage.



I II

Table I lists the major bands common to all six of these alkaloids, together with some of the bands of pyridine (*2*). Since the pyridine ring is common to all of these alkaloids, it is to be expected that many of their vibrational frequencies should correspond with pyridine frequencies. No simple assignment of bands to the five-membered ring in these alkaloids can be made from this small number of compounds. Although Pleat, Harley, and Wiberley (*5*) have proposed using the 13.966-micron (716 K.) band of nicotine for analytical purposes, Table I shows that a band near this location is characteristic of all these alkaloids containing the pyridine ring. This band corresponds to the strongest fundamental vibration of the pyridine spectrum (*2*).

EXPERIMENTAL

Methods of preparation and purification of these compounds have been described (*9*). Figures 1 and 5 were obtained with a Beckman IR-2 spectrophotometer, using the slit-drive mechanism suggested by Shreve and Heether (*6*). The transmittances were obtained by the method of Willis and Philpotts (*10*). Figures 2, 3, 4, and 6 were obtained with a Beckman IR-3 spectrophotometer, which records transmittance directly and has considerably higher resolution. Sodium chloride prisms were used in both instruments.

The term "kayser" (K.) is used in this paper as a unit of wave number, as recommended by the Joint Commission for Spectroscopy (*1*).

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