form (24 mg., m.p. 196–198°, identified by comparison with an authentic specimen; C) coreopsin, obtained in crystalline form (18 mg.), m.p. 213–214°, and sulfurein; and D) additional okanin, from which 50 mg. of crystalline material was isolated, and maritimetin.

Band D, after elution and concentration of the eluate to 5 ml., yielded 309 mg. of marein. This was crystallized as bright orange aggregates from 50% ethanol. When hydrolyzed with 5% hydrochloric acid it gave a mixture of okanin and the isomeric flavano-okanin. The presence of marein in the mother liquors was readily established by paper chromatographic comparison with authentic material and by spectral measurements.

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LOS ANGELES, CALIF.

[CONTRIBUTION FROM THE LABORATORY OF CHEMISTRY OF NATURAL PRODUCTS, NATIONAL HEART INSTITUTE, NATIONAL INSTITUTES OF HEALTH, U. S. PUBLIC HEALTH SERVICE, DEPARTMENT OF HEALTH, EDUCATION AND WELFARE]

Alkaloids of *Ormosia jamaicensis* (Urb.)—Jamaicensine and Jamaidine

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Jamaicensine, $C_{14}N_{22}N_2O$, and jamaidine, $C_{15}H_{24}N_2O_2$, have been isolated from seeds of *Ormosia jamaicensis* (Urb.) and *O. panamensis* (Benth.) Jamaicensine closely resembles, but may not be identical with, a new alkaloid angustifoline isolated recently from *Lupinus angustifolius*. Jamaidine is isomeric with hydroxylupanine but not identical with it.

Three isomeric bases of formula $C_{20}H_{33}N_3$ present in seeds of *Ormosia panamensis* (Benth.) and other *Ormosia* species were described in a previous paper.[1] Several additional alkaloids, two of which were oxygen-containing, were also found in seeds of *Ormosia* species which were examined, except for *O. stipitata* (Schery).[2] The oxygen-containing alkaloids have now been isolated and characterized. Seeds of *O. panamensis* and *O. jamaicensis* (Urb.) were used as the source of these compounds. The extraction process was carried out as described previously,[1] in such a way as to yield an ether solution that contained the three major bases (panamine, ormosanine, ormosinine) and a chloroform solution that contained two major components and several minor ones. Chromatography on alumina provided these two components in pure form. They were named jamaicensine and jamaidine.

Jamaicensine (m.p. 80.5–81°) was found to have an empirical formula $C_{14}H_{22}N_2O$ through analysis of the base and a number of derivatives. The hydrochloride and picrate were formed in 1:1 ratio of acid to base, and a determination of the neutral equivalent showed that only one basic group was present. A strongly positive Simon test indicated that this was a secondary amino group. This was confirmed through the preparation of an acetyl and a benzoyl derivative, and through the preparation of *N*-methyljamaicensine. The latter compound gave a negative Simon test. Additional analytical determinations indicated that one active hydrogen atom was present in the alkaloid, and that no C-methyl, *N*-methyl or *O*-methyl groups were present. No absorption was found through the ultraviolet region (above 220 mμ). The infrared absorption spectrum showed a strong carbonyl band at 1625 cm.$^{-1}$; this suggested that the oxygen atom was present in an amide group, possibly of the α-piperidone type. Strong absorption bands at 919 and 998 cm.$^{-1}$ and absorption at 3078 cm.$^{-1}$ in the carbon-hydrogen region suggested that a vinyl group $RCH{=}CH_2$ was present.[3] When the alkaloid was hydrogenated in acetic acid solution with platinum (Adams' catalyst), dihydrojamaicensine was formed. The infrared spectrum of this compound retained the carbonyl (amide) absorption band, but the bands at 3078 and 998 cm.$^{-1}$ were no longer present and only a weak band remained at 919 cm.$^{-1}$. Additional evidence for a terminal methylene group was obtained by oxidation of the alkaloid with a periodate-permanganate mixture; formaldehyde was isolated as the dimedone derivative.

The reduction of the ethylenic double bond and of the carbonyl (amide) group was effected in hydrochloric acid solution with a platinum catalyst. Dihydrodesoxyjamaicensine contained no oxygen and the infrared spectrum showed no evidence of a carbonyl or a terminal methylene group. This reduction method is applicable to lactams of the sparteine family.[4] The sum of evidence suggests that jamaicensine is a tricyclic base containing a lactam group, a secondary amino group, and a side chain with a vinyl group.

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(1) H. A. Lloyd and E. C. Horning, *J. Am. Chem. Soc.*, **80**, 1506 (1958).

(2) H. A. Lloyd and E. C. Horning, *J. Org. Chem.*, **23**, 1074 (1958).

(3) W. F. Cockburn and L. Marion, *Can. J. Chem.*, **30**, 92 (1952); L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, 2nd Edition, John Wiley and Sons, N. Y., 1958, p. 34.

(4) F. Galinovsky and E. Stern, *Ber.* **77**, 132 (1944).

Wiewiorowski, Galinovsky, and Bratek[5] recently reported the isolation of a new lupine alkaloid, angustifoline, from *Lupinus angustifolius* and *L. perennis*. This compound was reported to contain both a tertiary amino group and an amide group. The empirical formula of angustifoline is the same as that of jamaicensine, and there is a very close correspondence in the properties of the derivatives of angustifoline and those found for jamaicensine. A comparison of the pertinent data is given in Table 1. The extent of agreement suggests strongly that the two alkaloids may be identical, but the evidence for a secondary amine structure in jamaicensine is unequivocal. The two names should be retained until angustifoline can be reinvestigated.

TABLE I

PROPERTIES OF ANGUSTIFOLINE AND JAMAICENSINE DERIVATIVES

Angustifoline $C_{14}H_{22}N_2O$	Jamaicensine $C_{14}H_{22}N_2O$
M.p. 79–80°	M.p. 80.5–81°
$[\alpha]_D^{20}$ −7.5° (EtOH)	$[\alpha]_D^{25}$ +5.2 (EtOH)
$C_{14}H_{22}N_2O \cdot HCl \cdot H_2O$ m.p. 134–135°	$C_{14}H_{22}N_2O \cdot HCl$ m.p. 96–97°
Monopicrate m.p. 186°	Monopicrate m.p. 182–185°
Dihydroangustifoline	Dihydrojamaicensine
M.p. 82–83°	M.p. 82.5–83.5°
$[\alpha]_D^{20}$ +36.8° (EtOH)	$[\alpha]_D^{23}$ +37.2° (EtOH)
Dihydrodesoxyangustifoline	Dihydrodesoxyjamaicensine
Dipicrate m.p. 207° dec.	Dipicrate m.p. 204–210° dec.

Jamaidine, (m.p. 194.5–195°) was found to have an empirical formula $C_{15}H_{24}N_2O_2$. Analytical determinations indicated that an active hydrogen atom was present, and that C-methyl, *O*-methyl and *N*-methyl groups were absent. The Simon test was negative. A neutral equivalent determination indicated that only one nitrogen atom was present in a basic group. No absorption was found in the ultraviolet region (above 220 mμ). The infrared spectrum contained a strong band at 1625 cm.$^{-1}$ indicative of a carbonyl (amide) group. Bands at 3620 cm.$^{-1}$ and 3425 cm.$^{-1}$ were indicative of an hydroxyl group (nonbonded and bonded). An acetyl derivative was prepared.

Jamaidine was not reduced with a platinum catalyst in ethanol, and *O*-acetyl-jamaidine was not reduced with a platinum catalyst in acetic acid. When jamaidine was hydrogenated in hydrochloric acid solution with a platinum catalyst, the product was a base with an empirical formula $C_{15}H_{26}N_2O$. This substance showed no carbonyl (amide) absorption in the infrared spectrum, but the hydroxyl absorption bands were unchanged.

(5) M. Wiewiorowski, F. Galinovsky, and M. D. Bratek, *Monatsh.*, **88**, 663 (1957).

The structural information suggested that jamaidine was a hydroxylactam, probably of the sparteine or matrine group. The hydroxyl group was removed by Galinovsky's method,[6] and the product (after hydrogenation) had an infrared spectrum identical with that of an authentic specimen of *dl*-lupanine, and the molecular rotation was identical with that of *d*-lupanine. However, jamaidine is not identical with 13-hydroxylupanine, the only known naturally-occurring hydroxylupanine. The melting points, infrared spectra, and perchlorates of the two alkaloids are different and desoxyjamaidine does not correspond to 13-hydroxysparteine, the reduction product of the alkaloid, hydroxylupanine. Additional studies on both alkaloids are in progress.

EXPERIMENTAL[7]

Extraction. Seeds of *Ormosia jamaicensis* (1500 g.), processed in the manner reported in a previous paper,[1] yielded 35 g. of crude material from an ether extract and 8.1 g. of material from a chloroform extract. The two residues were examined by ascending paper chromatography on Whatman #1 paper, in a solvent system of *sec*-butyl alcohol, hydrochloric acid, and water (100:20:36). The ether extract consisted of a mixture of ormosinine, ormosanine, and panamine as described previously,[1] with traces of other bases. The chloroform extract was mostly jamaicensine (*Rf* 0.84) and jamaidine (0.60) and smaller amounts of alkaloids of *Rf* 0.32, 0.40 (ormosinine), 0.52 (panamine), 0.69 (ormosanine), and 0.96.

An extraction of *Ormosia panamensis* seeds gave substantially the same results.

Isolation of jamaicensine and jamaidine. The crude alkaloids of the chloroform extract were dissolved in dry thiophene-free benzene and chromatographed on Merck alumina (400 g.). The separation was followed by paper chromatography in the solvent system described above. Some nonbasic material was eluted with benzene. Elution with benzene–ethyl acetate (3:1) and benzene–ethyl acetate (3:2) gave 1.55 g. of a mixture of alkaloids of *Rf* 0.30, 0.43, 0.54, 0.68, and increasing amounts of jamaicensine (0.84). Elution with benzene–ethyl acetate (2:3) and pure ethyl acetate gave 2.45 g. of a semicrystalline fraction consisting of jamaicensine with traces of other alkaloids. Several recrystallizations from hexane yielded 2.1 g. of jamaicensine, m.p. 78–80°. Continued elution of the column with ethyl acetate and ethyl acetate–chloroform (9:1) gave 1.34 g. of an oily mixture of jamaicensine and jamaidine (*Rf* 0.60). Upon addition of ether to this oil, jamaidine (0.65 g.) crystallized as small needles, m.p. 185–188°. Elution with chloroform gave a brown oil (0.75 g.), a mixture of jamaicensine, jamaidine, and an alkaloid of *Rf* 0.98. Further chromatography of the intermediate fractions yielded small amounts of jamaicensine and jamaidine.

Jamaicensine. The material obtained by column chromatography was sublimed at 60° (0.001 mm.) and recrystallized twice from hexane to give clusters of short needles, m.p. 80.5–81°, $[\alpha]_{589}^{25}$ +5.2°, $[\alpha]_{436}^{25}$ +20.4° (*c* 0.95, ethanol).

Anal. Calcd. for $C_{14}H_{22}N_2O$: C, 71.75; H, 9.46; N, 11.96; neut. equiv., 234.3; active H, 0.43 (one), (C)CH_3, 6.42.

(6) F. Galinovsky and M. Pöhm, *Monats.*, **80**, 864 (1949).

(7) All melting points were observed on a Kofler stage. The optical rotations were taken with a Rudolph photo-electric spectropolarimeter and the infrared spectra were recorded on a Perkin-Elmer Model 21 or a Beckman IR-7 double-beam spectrophotometer. Analyses were performed by Mr. J. F. Alicino, Metuchen, N. J., and Mr. W. Manser, Zurich, Switzerland.

Found: C, 71.54; H, 9.37; N, 11.61; neut. equiv., 238; active H, 0.50; OCH_3, none; (C)CH_3, 1.22; (N)CH_3, none.

Jamaicensine hydrochloride. A solution of jamaicensine in ethanol was made acid to Congo Red by addition of a few drops of concd. hydrochloric acid. The hydrochloride was precipitated by addition of ether and was recrystallized from acetone containing a drop of methanol; it formed fine needles, m.p. 96–98°, $[\alpha]_{589}^{23}$ +15°, $[\alpha]_{436}^{23}$ +39° (*c* 0.92 ethanol).

Anal. Calcd. for $C_{14}H_{22}N_2O\cdot HCl$: C, 62.09; H, 8.56; N, 10.35; Cl, 13.09. Found: C, 61.95; H, 8.58; N, 10.24; Cl, 13.21.

Jamaicensine picrate was prepared by treating the free base in ether with an excess of a saturated ether solution of picric acid. The precipitate was washed with ether and recrystallized twice from ethanol, m.p. 182–185° dec.

Anal. Calcd. for $C_{14}H_{22}N_2O\cdot C_6H_3N_3O_7$: C, 51.83; H, 5.44; N, 15.11. Found: C, 51.90; H, 5.43; N, 15.17.

N-Methyljamaicensine hydriodide was prepared by refluxing the free base in acetone with an excess of methyl iodide. It was recrystallized four times from acetone-ether to give needles, m.p. 196–199°.

Anal. Calcd. for $C_{15}H_{25}N_2OI$: C, 47.88; H, 6.70; N, 7.45; I, 33.73. Found: C, 47.56; H, 6.79; N, 7.46; I, 33.84.

N-Methyljamaicensine. A solution of the hydriodide in water was made strongly basic with sodium hydroxide and extracted exhaustively with chloroform. The chloroform extract yielded a crystalline residue which was sublimed and recrystallized twice from hexane to give iridescent plates, m.p. 90–91°.

Anal. Calcd. for $C_{15}H_{24}N_2O$: C, 72.54; H, 9.74; N, 11.28; neut. equiv., 248.4. Found: C, 72.80; H, 9.72; N, 11.32; Neut. equiv., 246.

N-Benzoyljamaicensine prepared by the Schotten-Baumann method was recrystallized three times from benzene-cyclohexane to give small prisms, m.p. 194.5–195.5°.

Anal. Calcd. for $C_{21}H_{26}N_2O_2$: C, 74.52; H, 7.74; N, 8.28. Found: C, 74.35; H, 7.81; N, 8.28.

N-Acetyljamaicensine. A solution of jamaicensine in acetic anhydride was allowed to stand overnight at room temperature. The excess anhydride was destroyed with water and the solution was neutralized with sodium carbonate and extracted with chloroform. Evaporation of the dried organic extract yielded a colorless sirup which crystallized on trituration with ether. Three recrystallizations from cyclohexane-ether gave thick needles, m.p. 150.5–151.5°.

Anal. Calcd. for $C_{16}H_{24}N_2O_2$: C, 69.53; H, 8.75; N, 10.14. Found: C, 69.59; H, 8.80; N, 10.10.

Dihydrojamaicensine. A solution of 240 mg. of jamaicensine in 15 ml. of glacial acetic acid was added to 15 ml. of acetic acid containing 70 mg. of reduced platinum oxide catalyst, and the mixture was stirred under hydrogen at room temperature and atmospheric pressure. The reduction stopped in 10 min. after 1 equivalent of hydrogen was absorbed. The solution was filtered from the catalyst and evaporated to dryness *in vacuo*. The residue was dissolved in a small amount of water and the solution was made strongly alkaline with sodium hydroxide pellets and extracted with ether and chloroform. The combined extracts, when dried and evaporated, yielded 211 mg. of thick oil which crystallized to a buff-colored product on trituration with a few drops of ether. The material was sublimed at 60° (0.001 mm.) and recrystallized from hexane to give colorless prisms, m.p. 82.5–83.5°, $[\alpha]_{589}^{23}$ +37.2°, $[\alpha]_{436}^{23}$ +90.3° (*c* 1.24, ethanol).

Anal. Calcd. for $C_{14}H_{24}N_2O$: C, 71.14; H, 10.24; N, 11.85; (C)CH_3, 6.36; neut. equiv., 236.3. Found: C, 71.09; H, 10.21; N, 11.75; (C)CH_3, 2.98; neut. equiv., 233.

Dihydrojamaicensine hydrochloride was prepared in ethanol-ether and recrystallized twice from wet acetone to give fine long needles, m.p. 89–90.5°.

Anal. Calcd. for $C_{14}H_{24}N_2O\cdot HCl\cdot H_2O$: C, 57.81; H, 9.36; N, 9.63; Cl, 12.19; (C)CH_3, 5.17. Found: C, 57.66; H, 9.30; N, 9.68; Cl, 12.09; (C)CH_3, 2.93.

Hydrogenation of jamaicensine with platinum in dilute hydrochloric acid. A solution of 238 mg. of jamaicensine in 20 ml. of 1*N* hydrochloric acid was stirred under hydrogen with 250 mg. of reduced platinum oxide catalyst. The reduction stopped in 5 hr. after 3 equivalents of hydrogen were absorbed at room temperature and atmospheric pressure. The catalyst was removed by filtration and the solution was made strongly basic with sodium hydroxide pellets and extracted with chloroform to yield 225 mg. of thick colorless oil.

Dipicrate of dihydrodesoxyjamaicensine. A solution of the oil in ether was treated with an ether solution of picric acid and the precipitate was recrystallized three times from ethanol to give small needles, m.p. 204–210° dec.

Anal. Calcd. for $C_{14}H_{26}N_2\cdot 2C_6H_3N_3O_7$: C, 45.88; H, 4.74; N, 16.47. Found: C, 45.91; H, 4.63; N, 16.22.

Oxidation of jamaicensine with potassium permanganate–periodic acid. An aqueous solution of periodic acid (30 mg.) was added to a solution of 30 mg. of jamaicensine and a crystal of potassium permanganate in 10% acetic acid. The brown solution was allowed to stand for 10 min. and filtered through charcoal. A solution of 30 mg. of dimedone in 50% aqueous alcohol was added and the mixture was heated for 2 min. (water bath). Upon standing fine long needles separated. The product was recrystallized from aqueous alcohol, and the m.p. and mixed m.p. with an authentic sample of dimedone derivative of formaldehyde was 189–191°.

Jamaidine. Sublimation of the crude product followed by repeated recrystallizations from acetone yielded colorless needles, m.p. 194.5–195°, $[\alpha]_{589}^{23}$ +63.7°, $[\alpha]_{436}^{23}$ +141° (*c* 0.66, ethanol).

Anal. Calcd. for $C_{15}H_{24}N_2O_2$: C, 68.15; H, 9.15; N, 10.60; active H, 0.38 (one); neut. equiv., 264.4. Found: C, 67.91, 68.02; H, 9.30, 9.15; N, 10.78, 10.70; active H, 0.31; neut. equiv., 267; (N)CH_3, none; (C)CH_3, none; OCH_3, none.

Jamaidine perchlorate. This salt was prepared and recrystallized from methanol; it formed small prisms, m.p. 175–177°.

Anal. Calcd. for $C_{15}H_{24}N_2O_2\cdot HClO_4$: C, 49.38; H, 6.91; N, 7.68; Cl, 9.72; neut. equiv., 364.8. Found: C, 49.42, 49.57; H, 6.81, 6.71; N, 7.59, 7.74; Cl, 9.66, 9.77; neut. equiv., 366.

O-Acetyljamaidine. A solution of jamaidine in acetic anhydride and pyridine was heated for 10 min. (steam bath). The excess anhydride was decomposed with water, and the solution was made strongly basic with sodium hydroxide and extracted with chloroform. The chloroform extract was dried over anhydrous potassium carbonate and concentrated *in vacuo* to give a pale yellow oil which crystallized upon trituration with ether. Two recrystallizations from acetone gave colorless plates, m.p. 170.5–171°. The acetate showed basic properties.

Anal. Calcd. for $C_{17}H_{26}N_2O_3$: C, 66.64; H, 8.55; N, 9.14. Found: C, 66.71; H, 8.52; N, 9.08.

Hydrogenation experiments. A solution of *O*-acetyl jamaidine in acetic acid was stirred for 2 hr. under hydrogen with reduced platinum oxide. No hydrogen was absorbed at room temperature and atmospheric pressure and the base was recovered unchanged. Under similar conditions a solution of jamaidine in ethanol did not absorb hydrogen.

Desoxyjamaidine. A mixture of 136 mg. of jamaidine and 140 mg. of reduced platinum oxide catalyst in 1*N* hydrochloric acid absorbed 2 equivalents of hydrogen in 12 hr., at room temperature and atmospheric pressure. The solution, filtered from the catalyst, was made strongly alkaline and thoroughly extracted with chloroform. The extract was dried and evaporated to yield 124 mg. of colorless crystals, m.p. 174–177°. Two recrystallizations from acetone gave long needles, m.p. 178–179°, $[\alpha]_{589}^{24}$ −25.6°, $[\alpha]_{436}^{24}$ −47.3° (*c* 0.76, ethanol).

Anal. Calcd. for $C_{15}H_{26}N_2O$: C, 71.95; H, 10.47, N, 11 19; neut. equiv. 125.3. Found: C, 72.03; H, 10.37; N, 11.04; neut. equiv., 125.3.

The *dipicrate* of desoxyjamaidine was prepared in ethanol

and recrystallized from ethyl acetate–ethanol, m.p. 122° dec.

Anal. Calcd. for $C_{15}H_{26}N_2O \cdot 2C_6H_3N_3O_7$: C, 45.76; H, 4.55; N, 15.81. Found: C, 46.00; H, 4.84; N, 15.52.

Conversion of jamaidine to d-lupanine. A mixture of 100 mg. of jamaidine and 1 g. of phosphorus pentoxide was heated for 6 hr. at 170–180° under nitrogen. It was then cooled to room temperature and ice water was added to decompose the phosphorus pentoxide. The resulting solution was made strongly basic with potassium hydroxide and extracted with chloroform. The extract was dried, the solvent was evaporated, and the residue was submitted to evaporative distillation in high vacuum (0.01 mm.). A colorless oil (45 mg.) was obtained. The infrared spectrum carbon tetrachloride showed a band at 3021 cm.$^{-1}$ (—CH=CH—) and no hydroxyl absorption. The oil was dissolved in absolute ethanol and hydrogenated at room temperature and atmospheric pressure in the presence of 10% palladium-charcoal catalyst. The solution took up the calculated amount of hydrogen in 5 min. After another 15 min., during which no more hydrogen was absorbed, the catalyst was removed by filtration and the solution was evaporated. Two evaporative distillations of the residue yielded 35 mg. of thick colorless oil, $[\alpha]^{24}_{589}$ +78.5 (*c* 0.35, ethanol); the reported[8] rotation of *d*-lupanine is $[\alpha]^{20}_{D}$ +79.5. The infrared spectrum of the product was identical with that of an authentic sample of *dl*-lupanine. A picrate, m.p. 180–183° was prepared; the reported[8] melting point of *d*-lupanine picrate is 185°.

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(8) J. F. Couch, *J. Am. Chem. Soc.*, 59, 1469 (1937).

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH, PUBLIC HEALTH SERVICE, U. S. DEPARTMENT OF HEALTH, EDUCATION, AND WELFARE]

Chemistry of the Spiroaminoketal Side Chain of Solasodine and Tomatidine. IV.[1] Chemistry of the Tomatidine Side Chain

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Treatment of tomatidine with acetic anhydride yields an acetylated Δ^5-tetrahydropyridylallopregnane and a diacetylamino-5α,20(22)furostene derivative. With a zinc chloride-acetic anhydride-acetic acid solution tomatidine affords a Δ^1-tetrahydropyridylallopregnane derivative. The chemistry of these compounds is discussed.

In the previous papers of this series, solasodine and its derivatives were subjected to a series of reactions which revealed the interesting and interrelated chemistry of the spiroaminoketal system present in these alkaloids. Tomatidine has now been exposed to a similar series of reactions and, as expected, behaves in an analogous manner. The acetic anhydride treatment of tomatidine[3] (I. R = H) yields the crystalline 26-aminodiacetyl-5α-furost-20(22)en-3β-ol acetate (II) and an amorphous component which affords crystalline III. The oxidation and subsequent removal of the 16β-aminodiacetyl ester side chain of II to Δ^{16}-allopregnenolone (VI. R = H) have previously been reported.[3] The oxidative degradation to 3β-acetoxyallopregnenolone (VI. R = Ac) of the 26-aminoacetyl derivative V which is readily obtained from II by chromatography on an alumina column or from the acid catalyzed isomerization of *O,N*-diacetyltomatidine (Ia. R = Ac) has similarly been described.[4] The reversion of V to II can be effected by treatment of V with a solution of acetic anhydride and pyridine.

The above mentioned amorphous residue, obtained from the acetic anhydride treatment of tomatidine, possesses an ultraviolet absorption band at 236 mμ (log ϵ, 3.92) and characteristic infrared absorption bands at 5.78, 5.98, and 6.07 μ. These data are in close agreement with those obtained for the analogous product from solasodine[5] and are consistent for the assignment of an α,β-unsaturated acetylamino function[6,7] to this component. This is supported by the correct elemental analysis[4] (for structure III) as well as by the following transformation. Hydrolysis of the amorphous mass with hydrochloric acid in acetic acid yields the crystalline acetylamino ketone IV as in

(1) For previous papers of this series see *J. Org. Chem.*, 25, 789 (1960).

(2) Visiting Scientist, National Institutes of Health.

(3) Y. Sato, A. Katz, and E. Mosettig, *J. Am. Chem. Soc.*, 74, 538 (1952).

(4) See Part I, Y. Sato, N. Ikekawa, and E. Mosettig, *J. Org. Chem.*, 25, 783 (1960).

(5) See Part II, Y. Sato and N. Ikekawa, *J. Org. Chem.*, 25, 786 (1960).

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(7) R. Griot and T. Wagner-Jauregg, *Helv. Chim. Acta*, 42, 121, 605 (1959).