509. *The Isolation and Characterisation of the Alkaloids of* Ormosia jamaicensis *Urb.*

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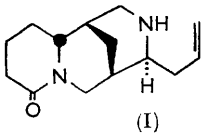
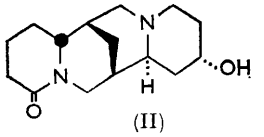
The mixture of alkaloids in the seeds of *Ormosia jamaicensis* Urb contains piptamine ($C_{20}H_{35}N_3$), angustifoline ($C_{14}H_{22}N_2O$), and three new bases ormojanine ($C_{20}H_{31}N_3$), ormosajine ($C_{20}H_{33}N_3$), and ormojine ($C_{20}H_{33}N_3$). The relationships of these bases to alkaloids in *Piptanthus nanus* and in other *Ormosia* species is discussed. Two other minor alkaloids have been shown to be present in the mixture of bases.*

Although interesting biological properties have long been attributed to extracts of *Ormosia* species, until recently little effort has been applied to the investigation of the active constituents. Hess and Merck [2] reported that seeds of *Ormosia dasycarpa* Jacks contained ormosine. $C_{20}H_{33}N_3,3—4H_2O$, m. p. 85—87°, an alkaloid with a strong analgesic action, together with an isomer, ormosinine, m. p. 203—205°. However, the work attracted little attention until 1956, when Moran and his co-workers [3] showed that an alkaloidal preparation from the seeds of *O. panamensis* Bent] was oxidised in air to a product with a profound hypotensive action on dogs. This was followed by investigations of the alkaloidal constituents of the seeds of various species of *Ormosia*. Paper chromatography studies by Lloyd and Horning [4] on nine species indicated that six alkaloids commonly occurred in members of the family and, in the case of *O. jamaicensis*, a seventh base was detected. *O. stipitata* was atypical; it produced only one alkaloid which was identified as *N*-methylcytisine.[5]



(I)



(II)

Experiments directed towards isolation of the bases have been carried out on three species. Three isomeric compounds, $C_{20}H_{33}N_3$, were prepared by Lloyd and Horning from seeds of *O. panamensis*.[4] One, m. p. 219—220°, was thought to be identical with ormosinine; another, m. p. 167—168°, was named ormosanine, while the major constituent, m. p. of hydrate 38—40°, was given the name panamine. When Clarke and Grundon re-examined the seeds of *O. dasycarpa* neither ormosine nor ormosinine was found.[6] Sparteine, a new amorphous base, $C_{20}H_{35}N_3$, which was named dasycarpine, and a crystalline compound, first assigned the formula $C_{20}H_{37}N_3O_3$ but later identified as dasycarpine

* A preliminary account of part of this work has been published.[1]

[1] Hassall and Wilson, *Chem. and Ind.*, 1961, 1358.
[2] Hess and Merck, *Ber.*, 1919, **52**, 1976.
[3] Moran, Quinn, and Butler, *Fed. Proc.*, 1956, **15**, 462; 1957, **16**, 324; Quinn, Butler, and Moran, *Fed. Proc.*, 1956, **15**, 470.
[4] Lloyd and Horning, *J. Amer. Chem. Soc.*, 1958, **80**, 1508.
[5] Lloyd and Horning, *J. Org. Chem.*, 1958, **23**, 1074.
[6] Clarke and Grundon, *J.*, 1960, 41.

hydrochloride,[7] were isolated. During the course of the current study, Lloyd and Horning reported an investigation on *O. jamaicensis* Urb.[8] An extraction process similar to that used for *O. panamensis* led to the isolation of two pure bases which were named jamaicensine ($C_{14}H_{22}N_2O$) and jamaidine ($C_{15}H_{24}N_2O_2$). Subsequent investigations [1,9] identified these compounds as angustifoline (I), an alkaloid recently isolated from several *Lupinus* species,[10,11] and 13-epihydroxylupanine (II) which has been prepared from angustifoline by the action of formaldehyde in acid solution.[12] It was also suggested,[4] on the basis of paper chromatography alone, that ormosanine, ormosinine and panamine were present in the mixture of alkaloids from *O. jamaicensis*.

The present investigation was prompted by an interest in the unusual biological activity attributed to some of the bases from *Ormosia* species and the indication from the work of Hess and Merck that a novel group of alkaloids was involved. Preliminary studies, carried out in this laboratory by Evans,[13] pointed the way towards a successful separation of the mixture of bases which occurred to the extent of approximately 2·25% in the seeds of *O. jamaicensis*. The procedure that was finally adopted involved extraction of a basified aqueous solution of the mixture of alkaloids with ether and chloroform, in turn. The chloroform extract was a rich source of angustifoline (I) which was identified through the preparation of derivatives and comparison with authentic material kindly supplied by Professor M. Wiewiorowski. One of the bases in the ether extract separated

TABLE 1.

	Ormosanine [4]	Piptamine [14]	Base from *O. jamaicensis*
Molecular formula	$C_{20}H_{33}N_3$	$C_{14}H_{24}N_2$	$C_{20}H_{35}N_3$
M. p.	167—168°	173—174°	178°
$[\alpha]_D$	+3·3°	0°	1 ± 3°
M. p. of base, 2HI	249°	—	—
M. p. of base, 3HI	—	—	268°
M. p. of *N*-methyl-derivative	—	96·5—97·5°	106°
M. p. of formaldehyde-derivative	—	147—148°	146°

in a crystalline form from the concentrated solution. Although some of its properties resembled those of ormosanine there were also notable differences (Table 1). On the other hand, the characteristics of our compound were very similar to those of piptamine, a base from *Piptanthus nanus* to which has been ascribed the formula $C_{14}H_{24}N_2$.[14] The two compounds were shown to be identical by direct comparison. Moreover, new evidence, including the mass spectrum of the base and analytical data on both the base and its derivatives, established the molecular formula for piptamine as $C_{20}H_{35}N_3$. This base was not susceptible to catalytic hydrogenation. The formation of derivatives indicated that the molecule had two secondary and one tertiary amino-group.[15] It gave a di-*N*-nitroso-derivative and an *N*-methyl-*N*-tosyl-derivative, and condensed with formaldehyde to give the compound $C_{21}H_{35}N_3$, which no longer contained secondary amino-groups. It is significant that the formula $C_{14}H_{24}N_2$, originally assigned to piptanthine, a base of m. p. 142—143°, that accompanies piptamine in *Piptanthus nanus*, has recently been corrected to $C_{20}H_{35}N_3$.[16] Moreover, some chemical properties of piptanthine, notably the formation of a derivative with formaldehyde, resemble those of some of the C_{20} alkaloids that have been isolated in this study.

[7] Clarke and Grundon, *J.*, 1963, 535.
[8] Lloyd and Horning, *J. Org. Chem.*, 1960, **25**, 1959.
[9] Lloyd, *J. Org. Chem.*, 1961, **26**, 2143.
[10] Wiewiorowski, Galinovsky, and Bratek, *Monatsh.*, 1957, **88**, 663.
[11] Bohlmann and Winterfeldt, *Chem. Ber.*, 1960, **93**, 1956.
[12] Marion, Wiewiorowski, and Bratek, *Tetrahedron Letters*, 1960, No. 19, 1.
[13] Evans, M.Sc. Thesis, University of Wales, 1958.
[14] Konovalova, Diskina, and Rabinovich, *Zhur. obshchei Khim.*, 1951, **21**, 773; *Doklady Akad. Nauk S.S.S.R.*, 1951, **78**, 705; Diskina and Konovalova, *ibid.*, 1951, **81**, 1069.
[15] Gibbon and Hassall, unpublished.
[16] Eisner and Šorm, *Coll. Czech. Chem. Comm.*, 1959, **24**, 2348.

TABLE 2.

	Panamine [4]	Ormosine [2]	Ormosajine
Molecular formula	$C_{20}H_{33}N_3$	$C_{20}H_{33}N_3$	$C_{20}H_{33}N_3$
$[\alpha]_D$	−13°	—	+23°
M. p. of $C_{20}H_{33}N_3,4H_2O$	38—40°	85—87°	38—41°
M. p. of base, $2HClO_4$	283—285°	—	170—171°
Catalytic hydrogenation in acid	No reaction	—	Uptake, 1 mol.

Further separation of the mixture of bases in the ether extract was achieved largely through countercurrent distribution. It was found that use of the system methanol–cyclohexane–ethyl acetate–water (5 : 5 : 5 : 1) led to the isolation of three new alkaloids. The base, m. p. 126°, $C_{20}H_{31}N_3$, to which we have assigned the name ormojanine, gave a diperchlorate and a tripicrate monohydrate. Catalytic hydrogenation in acid solution gave a dihydro-derivative which reacted with formaldehyde to form an adduct, $C_{21}H_{33}N_3$.

Another alkaloid, which we have named ormosajine, was obtained as a crystalline hydrate, $C_{20}H_{33}N_3,4H_2O$, m. p. 38—41°. As Lloyd and Horning [4] have isolated a hydrate, m. p. 38—40°, from *O. panamensis*, it seemed likely, at first, that their compound panamine was identical with ormosajine. However, the data in Table 2 show that panamine, ormosine, and ormosajine are different. Catalytic hydrogenation of ormosajine gave a dihydro-derivative which formed an adduct on treatment with formaldehyde. Comparison of the properties of derivatives of dihydro-ormosajine and dasycarpine, the major alkaloid isolated from *O. dasycarpa* by Clarke and Grundon, left little doubt that these compounds were identical. This was confirmed by comparison of the infrared spectra of the trihydrobromides of the two bases.

It has been posible to establish a relationship between ormosajine and the fifth crystalline compound isolated from the mixture of alkaloids. This minor base, $C_{20}H_{33}N_3$, m. p. 154°, which has been given the name ormojine, could also be obtained by treating ormosajine with dilute acid. Moreover, the action of dilute acid on ormojine led to the formation of an equilibrium mixture of ormosajine and ormojine. As dihydro-ormosajine is stable to acid, it appears likely that the isomeric alkaloids differ in the nature of their centres of unsaturation. Traces of two other alkaloids have been shown by paper chromatography to be present in the seeds of *O. jamaicensis*, but they have not been fully characterised.

The C_{20} bases piptamine, dihydro-ormojanine, dihydro-ormosajine(= dasycarpine), and piptanthine all have one tertiary amino-group, and two secondary amino-groups which react with formaldehyde. It seems evident that these bases, together with the $C_{20}H_{33-35}N_3$ compounds isolated from *O. panamensis*, constitute a new group of alkaloids that, from their occurrence with sparteine, angustifoline, and 13-epihydroxylupanine, may very well be related in molecular structure to the well-known quinolizidine alkaloids of *Leguminosae*.

EXPERIMENTAL

Ultraviolet absorption spectra were determined for ethanol solutions with a Unicam S.P. 500 spectrophotometer and an Optica CF4 recording spectrophotometer. Infrared absorption spectra were measured with a Grubb-Parsons GS2A spectrometer and a Perkin-Elmer Infracord instrument. Alumina for chromatography was Spence's grade H (100—200 mesh), which was kept under ethyl acetate for 2 days, filtered, washed with cyclohexane, and reactivated at 100° for 2 days.

Paper chromatography was on Whatman No. 1 paper using the following systems: system (I), butan-1-ol–hydrochloric acid–water (25 : 5 : 9, v/v); system (II), butan-2-ol–hydrochloric aci–water (25 : 5 : 9, v/v); system (III), butan-1-ol–acetic acid–water (4 : 1 : 5, v/v); system (IV), saturated aqueous ammonium sulphate–ethanol (75 : 1, v/v). R_F values refer to system I, unless otherwise defined. Dragendorff's reagent was used as a visualising spray.

Isolation of the Mixture of Alkaloids.—The experiments were on seeds of *O. jamaicensis* collected near Dolphin Head, Jamaica, during 1957. We are indebted to Drs. R. H. Burnell and R. F. Curtis for arranging the collection from almost inaccessible tropical forest and to

Messrs. Stafford Allen and Sons Ltd. for grinding the seeds. The procedure for the isolation of the alkaloids was based on exploratory studies due to D. Evans,[13] and further preliminary experiments which will not be described.

Ground seeds (19 kg.) were extracted in batches (3·8 kg.) in a modified Soxhlet apparatus, first with seven cycles of light petroleum (b. p. 60—80°), to remove fats, and then with ammonia (s.g. 0·88)–ethanol (1 : 10) until the extract gave no reaction for alkaloids with Dragendorff's reagent. The combined light petroleum extracts were concentrated to 2 l. and shaken with 50% aqueous ethanol (16 l.) to remove the alkaloids. The aqueous ethanol layer was applied to a column (12 cm. × 12 cm.) of the hydrogen form of the ion exchange resin, Dowex 50 × 4 (20—50 mesh, 1200 g.). The alkaloids, which were completely absorbed on the column, were eluted with ammonia (s.g. 0·88)–ethanol–water (2 : 5 : 5 : by vol.). The ethanol in the eluate was removed by distillation under reduced pressure to leave an aqueous suspension of alkaloidal material.

The ethanolic–ammonia extracts were concentrated at 30°, under reduced pressure, to remove ethanol. The concentrate (3·47 l.) was combined with the similar aqueous suspension (230 ml.) obtained from the light petroleum extract, adjusted to pH 2 with 0·1N-hydrochloric acid and extracted with methylene dichloride to remove non-alkaloidal material. The solution was adjusted to pH 10 by addition of concentrated ammonia solution and then extracted continuously with ether for 7 days. The extract was dried and evaporated to give a pale yellow gum (360 g.). Paper chromatography indicated the presence of at least six alkaloids:

R_F	0·21	0·32	0·41	0·56	0·77	0·94
Concn.*	2	10	10	2	1	1

* The concentration, measured visually, is represented by the scale 1—10.

The aqueous solution that remained was extracted, continuously, with chloroform for 3 days. The dried extract was evaporated to give a dark brown gum (79 g.) which was shown by paper chromatography to contain at least six bases:

R_F	0·21	0·32	0·41	0·56	0·77	0·94
Concn.*	1	10	10	1	7	1

Piptamine (with B. A. Gibbon).—The pale yellow gum (360 g.) from the ether extract of the aqueous suspension of alkaloids was dissolved in anhydrous ether (1,250 ml.) and left at 0° for 5 days. The crystals (6·34 g.; m. p. 174°) that separated were collected. The solution, concentrated to 500 ml., gave a yield of similar material (5·26 g.) after a further 3 weeks at 0°. The fractions were combined and recrystallised from ethyl acetate to give prisms, m. p. 178°; $[\alpha]_D^{20}$ +1° (*c* 1·00 in ethanol); $\lambda_{max.}$ 211 mμ (log ε 3·32); R_F 0·56 (system I), 0·68 (system II 0·38 (system III), 0·69 (system IV) [Found: C, 75·7; H, 11·2; N, 13·2%; *M* (mass spectrum), 317. Calc. for $C_{20}H_{35}N_3$: C, 75·7; H, 11·1; N, 13·2%; *M*, 317]. Piptamine, kindly provided by Dr. N. F. Proskurnina, had m. p. and mixed m. p. with our compound, 175—178°. The two preparations had identical infrared absorption spectra.

Angustifoline.—The gum from the chloroform extract (79 g.) in water–ethanol (7 : 3, 3 l.) was introduced into a column of the hydrogen form of the ion-exchange resin, Amberlite CG 120 (500 g.), at 500 ml./hr. After being washed with aqueous ethanol (2 l.), the alkaloids were eluted at 200 ml./hr. in 82 fractions (200 ml.) with 0·1N-ammonia solution in aqueous ethanol. Paper chromatography showed that fractions 38—82 (31·9 g.) contained a high concentration of the alkaloid, R_F 0·77, with similar proportions of ormosajine (R_F 0·41) and ormojanine (R_F 0·32), and traces of three alkaloids with R_F's 0·21, 0·56, 0·94.

The alkaloid, R_F 0·77, was isolated from this fraction by partition chromatography. The crude gum (5 g.), mixed with glass powder (50 g.), was packed on the top of a column (5 cm. × 50 cm.) prepared from Celite 545 which had been moistened with aqueous phosphate buffer (160 ml.) at pH 6·18 and then suspended in carbon tetrachloride. The column was eluted with carbon tetrachloride (2 l.), carbon tetrachloride–chloroform (9 : 1, 2 l.), and carbon tetrachloride–chloroform (8 : 2, 8 l.) in turn at a flow rate of 1·2 l./hr.; fractions of 1 l. were collected. Fractions 2—6 contained mixtures of alkaloids in varying proportions but fractions 7—12 contained one alkaloid (R_F 0·77) contaminated with traces of another (R_F 0·94). Evaporation of the solvent gave a gum (1·0 g.) which was further purified by chromatography on alumina, benzene being used as eluant, followed by recrystallisation from light petroleum (b. p. 80—100°) to yield

needles (217 mg.), m. p. 77°, $[\alpha]_D^{20}$ +7° (*c* 1·48 in ethanol); R_F 0·77 (system I), 0·87 (system II) 0·63 (system III), and 0·45 (system IV) [Found: C, 71·7; H, 9·25; N, 11·6%; *M* (Rast), 233. Calc. for $C_{14}H_{22}N_2O$: C, 71·8; H, 9·46; N, 12·0%; *M*, 234]. A sample of angustifoline kindly provided by Professor M. Wiewiorowski had m. p. and mixed m. p. with our compound, 77°; the samples had identical infrared absorption spectra. Moreover, angustifoline hydrochloride, m. p. 105°, angustifoline picrate, m. p. 187°, and 13-epihydroxylupanine were identical with similar derivatives of the base isolated in this study.

Ormosajine.—As in the case of the related compounds ormojine and ormojanine, ormosajine was isolated from the ether extract by countercurrent distribution. In a typical experiment, 15 g. of the crude alkaloids from this extract was distributed in the first 15 tubes of a 200-tube countercurrent apparatus (H. O. Post and Co., New York). The separation experiment utilised 10 ml. top and bottom phases of the solvent system methanol–cyclohexane–ethyl acetate–water (5 : 5 : 5 : 1; v/v). After 200 transfers (settling time 2 min.; complete cycle 5 min.; 50 sec.) the tubes were subjected to weight and paper-chromatography analyses. As tubes 0—59 contained substantial proportions of non-alkaloidal material the weights of alkaloids in these fractions were estimated by quantitative paper chromatography and must be regarded as approximate. The experimental and theoretical weight curves corresponding to the 7 alkaloids that were differentiated were plotted in the usual way.[17] Using these data and the equation: $N = nKr/(Kr + 1)$, where K is the partition ratio, N is the centre of gravity of the solute on the weight curve (expressed as tube no.), n is the total number of transfers and r is the ratio of volumes of phases, the results in Table 3 were obtained. $Y_{max.}$ is the weight of a given alkaloid in the tube N for that alkaloid.

The alkaloid, R_F 0·41, was obtained by withdrawing the contents of tubes 0—50 and 131—199, recycling (230 transfers), and selecting the fraction containing this base. This preparation from a number of countercurrent distribution experiments (30·21 g.) contained 95% of the single base contaminated with 3·5% of the base R_F 0·32 and 1·5% of the base R_F 0·21. It was purified by further countercurrent distribution (500 transfers with recycling) to give a gum that crystallised spontaneously. This product (23 g.) was recrystallised from moist ether to give rods, m. p. 38—41°, that lost weight on drying *in vacuo* to give a gum, $[\alpha]_D^{20}$ +23° (*c* 0·94 in ethanol); $\lambda_{max.}$ 212·5 mμ (log ε 3·42); R_F 0·41 (system I), 0·54 (system II), 0·42 (system III), and 0·54 (system IV) [Found: C, 76·1; H, 10·4; N, 13·5%; *M* (mass spectrum) 315. $C_{20}H_{33}N_3$ requires C, 76·1; H, 10·5; N, 13·3%; *M*, 315. Loss of weight on drying the hydrate, 19·0%. $C_{20}H_{33},N_3,4H_2O$ requires H_2O, 18·6%]. Analyses for *C*-methyl and *N*-methyl show that these groups are absent.

Ormosajine diperchlorate crystallised from ethanol as plates, m. p. 170—171° [Found: C, 46·1; H, 6·6; N, 8·1; O, 25·1; Cl, 13·8. $C_{20}H_{33}N_3,2HClO_4$ requires C, 46·5; H, 6·8; N, 8·1; O, 24·8; Cl, 13·7%]. The *picrate* was microcrystalline, m. p. 138—139° [Found: C, 47·6; H, 5·6; N, 15·3; O, 31·4. $C_{20}H_{33}N_3,2C_6H_3N_3O_7,2H_2O$ requires 47·5; H, 5·4; N, 15·6; O, 31·6%].

When ormosajine (794 mg.) in 0·1N-hydrochloric acid was shaken with Adams catalyst under hydrogen there was an uptake of 90·7 ml. (theoretical for 1 mol., 86·4 ml.). Working up in the usual way yielded a gum that distilled at 140°/0·1 mm. to give dihydro-ormosajine (750 mg.), m. p. 37—39°, $[\alpha]_D^{20}$ +12° (*c* 1·0 in ethanol) [Found: C, 75·7; H, 11·1; N, 12·8. Calc. for $C_{20}H_{35}N_3$: C, 75·7; H, 11·1; N, 13·2%]. Dihydro-ormosajine triperchlorate crystallised

TABLE 3.

Alkaloid R_F	0·21	0·32	0·41	0·56	0·65	0·77	0·94
N	158	84	113	130	68	37	55
K	3·76	0·72	1·30	1·86	0·52	0·23	0·38
$Y_{max.}$ (mg.)	20	177	209	51	5	10	5
Calc. wt./15 g. of extract (g.)	0·31	3·42	4·4	0·85	0·06	0·14	0·06

from ethanol as needles, m. p. 241—243° [Found: C, 39·0; H, 6·5; N, 6·4; O, 30·7; Cl, 16·6. Calc. for $C_{20}H_{35}N_3,3HClO_4$: C, 38·8; H, 6·2; N, 6·8; O, 31·1; Cl, 17·2%]. Dihydro-ormosajine picrate was purified by precipitation with ethanol from a concentrated solution in acetone. The amorphous powder had m. p. 152° (decomp.) [Found: C, 44·6; H, 4·6; N, 16·5; O, 34·4. Calc. for $C_{20}H_{35}N_3,3C_6H_3N_3O_7,H_2O$: C, 44·6; H, 4·5; N, 16·4; O, 34·4%]. Dihydro-ormosajine

[17] Craig and Craig, "Technique of Organic Chemistry," 2nd Edn., ed. Weissberger, Interscience Publ., New York, 1956, Vol. III, Part I, Chap. II.

trihydrobromide was prepared by the action of hydrogen bromide on dihydro-ormosajine in ethanol. It crystallised from ethanol–water as needles, m. p. 271—274° (decomp.) [Found: C, 39·3; H, 7·4. Calc. for $C_{20}H_{35}N_3,3HBr,3H_2O$: C, 39·1; H, 7·2%]. A sample dried at 60° under reduced pressure had m. p. 271—274° (decomp.) [Found: C, 43·9; H, 7·0; N, 7·5; Br, 42·0. $C_{20}H_{35}N_3,3HBr$ requires C, 44·1; H, 6·7; N, 7·3; Br, 41·9%]. The infrared spectrum of this compound was kindly compared on our behalf with that of dasycarpine trihydrobromide by Dr. M. F. Grundon. This confirmed that dasycarpine and dihydro-ormosajine are identical. Clarke and Grundon record m. p.s 240 and 150—152° for the perchlorate and picrate of dasycarpine.[6]

The *formaldehyde-adduct of ormosajine* was prepared by the action of 40% formalin (1 ml.) on dihydro-ormosajine (100 mg.) in acetic acid–water (1 : 3; 0·5 ml.) during 2 days at room temperature. After being heated on a water bath for 4 hr. the mixture was cooled and basified with ammonia go give a precipitate which sublimed at 128°/1 mm., m. p. 137—138°, $[\alpha]_D^{20}$ +10° (*c* 0·96 in ethanol), R_F 0·40 system I), 0·55 (system II), and 0·42 (system IV) [Found: C, 76·4; H, 10·9; N, 12·5%; *M* (Rast), 364. $C_{21}H_{35}N_3$ requires C, 76·5; H, 10·7; N, 12·8%; *M*, 329].

Ormojine.—The countercurrent distribution study on the ether extract of the crude mixture of alkaloids showed that the compound, R_F 0·21, had a partition ratio (*K*, 3·76) that differed very significantly from those of the other alkaloids in the mixture (Table 3). Paper chromatography studies on tubes 150—175 of the 200-transfer study confirmed that this alkaloid, alone, had accumulated in this fraction. The crude material (4·8 g.), obtained by evaporation of this fraction from several countercurrent runs, was recrystallised from acetone to yield *ormojine* as rhombs (2·96 g.), m. p. 154—155°, $[\alpha]_D^{20}$ +24° (*c* 1·46 in ethanol); $\lambda_{max.}$ 211 mμ (log ε 3·42); R_F 0·21 (system I), 0·33 (system II), 0·23 (system III), and 0·36 (system IV) [Found: C, 75·9; H, 10·5; N, 13·2%; *M* (mass spectrum), 315. $C_{20}H_{33}N_3$ requires C, 76·1; H, 10·5; N, 13·3%; *M*, 315]. A *picrate*, m. p. 182·5°, was obtained as an amorphous powder. [Found: C, 48·7; H, 4·95; N, 15·7; O, 30·6. $C_{20}H_{33}N_3,2C_6H_3N_3O_7,H_2O$ requires: C, 48·5; H, 5·2; N, 15·9; O, 30·3%].

There was an uptake of 1·03 mol. hydrogen when ormojine, in 0·1 N-hydrochloric acid, was reduced with hydrogen in the presence of Adams catalyst. The product, R_F 0·28 (system I), 0·37 (system II), 0·28 (system III), and 0·43 (system IV) was amorphous and could not be distilled without decomposition. It could not be characterised through the preparation of salts.

Interconversion of Ormojine and Ormosajine.—Experiments based on the identification of products by paper chromatography suggested that both ormojine and ormosajine could be converted into a mixture of isomers through the action of hydrochloric acid. This was confirmed through isolation experiments. Ormosajine hydrate (400 mg.) in ethanol (95 ml.) and 10N-hydrochloric acid (5 ml.) was boiled under reflux for 4 hr. Paper chromatography of the gum (310 mg.) obtained by concentrating to 3 ml., basifying with sodium hydroxide, extracting with chloroform, and evaporating the solvent, showed the presence of approximately equal amounts of two compounds with R_F's 0·21, 0·41. The compound, R_F 0·21, was obtained by recrystallisation of the gum (310 mg.) from acetone, as rhombs (25 mg.), $[\alpha]_D^{20}$ +22° (*c* 1·4 in ethanol), m. p. 152—155° undepressed on admixture with ormojine. The product had the same R_F values in systems I—IV and had an infrared spectrum identical with that of ormojine. The compound R_F 0·41 was isolated from a similar experiment as a gum with an infrared spectrum identical with that of ormosajine and the same R_F values in systems I—IV. When dihydro-ormosajine was refluxed with hydrochloric acid under similar conditions, paper chromatography studies showed that the starting material was not changed. However, when ormojine was heated with hydrochloric acid under these conditions approximately equal amounts of two compounds with R_F's 0·21 and 0·41 were in evidence after 2 hr.

Ormojanine.—The 430-transfer countercurrent distribution study described in the preparation of ormosajine gave a fraction that contained a high concentration (94%) of the compound R_F 0·32, contaminated notably with ormosajine and piptamine. Calculations based on information in Table 3 indicated that the alkaloid could be purified by countercurrent distribution with 400 transfers and recyling. The product of this procedure crystallised from light petroleum (b. p. 60—80°) as prisms, m. p. 126°, $[\alpha]_D^{20}$ −144° (*c* 0·75 in ethanol), $\lambda_{max.}$ 212·5 mμ (log ε 3·47); R_F 0·32 (system I), 0·47 (system II), 0·36 (system III), and 0·56 (system IV) [Found: C, 76·8; H, 9·9; N, 13·3%; *M* (mass spectrum), 313. $C_{20}H_{31}N_3$ requires C, 76·6;

H, 10·0; N, 13·4%; 313]. *Ormojanine diperchlorate* crystallised from ethanol as prisms, m. p. 256—257° (decomp.) [Found: C, 47·0; H, 6·7; N, 8·0; O, 24·8; Cl, 13·9. $C_{20}H_{31}N_3,2HClO_4$ requires C, 46·7; H, 6·5; N, 8·2; O, 24·9; Cl, 13·8%]. *Ormojanine tripicrate* crystallised from acetone as needles, m. p. 169—170° (Found: C, 45·1; H, 3·9; N, 16·6; O, 34·9. $C_{20}H_{31}N_3,3C_6H_3N_3O_7,H_2O$ requires C, 44·8; H, 4·2; N, 16·5; O, 34·6%).

Minor Alkaloids.—The countercurrent studies on the crude mixture of alkaloids gave a fraction (tubes 30—75 in the 200-transfer experiment) that contained angustifoline, ormojanine, and traces of two unidentified bases, A and B.

	R_F in system I	system II	system III	system IV
A	0·65	0·75	0·55	0·48
B	0·94	0·98	0·74	0·42

A mixture of alkaloids (2·2 g.) that was concentrated with respect to A and B by further countercurrent distribution (500 transfers with recycling) was used for repeated chromatography on alumina, light petroleum and benzene being used, in turn, as eluants. The fraction from the initial eluates (39 mg.) was an oil that appeared, from paper chromatography, to contain B, alone. Base A could not be obtained free from B but a gum (22 mg.) containing not more than 5% of B, was isolated from the later eluates. This preparation of A had an infrared spectrum indistinguishable from that of 13-hydroxylupanine (but different from that of 13-epihydroxylupanine), while B had a spectrum that was very similar apart from bands at 5·88 and 7·91 μ.

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