sample of camphor nitrimine also showed closely comparable infrared and ultraviolet absorption. In agreement with the formulation of the product as 3-nitriminofriedelane, it was readily converted to friedelin by heating in aqueous dioxane.

In terms of the proposed mechanism[7] of nitrimine formation by the action of nitrous acid, steric influences should favor attack of the NO^+ ion on the oxygen rather than the nitrogen atom of the oxime function. It has been recognized[7] that formation of nitrimines from oximes is, indeed, rather unusual and had previously been observed "only when the carbon atom on one side of the >C=N—OH group lacks hydrogen atoms." The example reported here indicates that this is not a strict structural requirement. Although the ketone group of friedelin is unhindered in the sense that it forms carbonyl derivatives under the usual conditions, it is unusual in forming the axial alcohol, epifriedelanol, in very high yield by metal hydride reduction. This has been attributed[3] to the influence of the axial methyl group at C_5. The combined effect of the equatorial methyl group at C_4 and the axial methyl group at C_5 conceivably serves to restrict attack of the NO^+ ion on the nitrogen atom of friedelin oxime.

EXPERIMENTAL

Friedelin oxime (II). (a). To a solution of sodium acetate (1.5 g.) and hydroxylamine hydrochloride (1.5 g.) in water (3 cc.), ethanol (20 cc.) was added. The mixture was filtered and the filtrate added to a solution of friedelin (5 g.) in benzene (100 cc.). After refluxing for 1 hr., water was added, the product collected by filtration and crystallized once from a large volume of benzene and once from dioxane to give friedelin oxime as plates (3.3 g.), m.p. 289–292° (softens at 283°), m.p. 298–302° (softens at 293°) in vacuum; lit.[6] value, m.p. 290–294°. (b) A solution of friedelin (200 mg., m.p. 255–262°) in pyridine (7 cc.) was added to hydroxylamine hydrochloride (200 mg.) in water (4 drops), the mixture refluxed for 45 min., cooled, and friedelin oxime (200 mg.) m.p. 289–292° (softens at 283°) collected as plates.

3-Nitriminofriedelane (III). Benzene (50 cc.) and acetic acid (50 cc.) were added to a suspension of friedelin oxime (925 mg.) in a 5% aqueous solution (50 cc.) of sodium nitrite. The mixture was allowed to stand with occasional shaking for 1 hr., the layers separated, and the benzene layer to which ether was added, washed with water, and dried (sodium sulfate). Removal of the solvents gave a white crystalline residue which was recrystallized from chloroform-methanol to give 3-nitriminofriedelane as felted needles (730 mg.), m.p. 224–226° dec., unchanged on further recrystallization, $[\alpha]_D$ +32° (c, 2.2 in chloroform). (Found: C, 76.43; H, 11.17; N, 6.42. $C_{30}H_{50}O_2N_2$ requires C, 76.54; H, 10.71; N, 5.95%), $\lambda_{max}^{C_2H_5OH}$ 2690 Å (ϵ 760). Infrared absorption (in chloroform): 1623 (m.), 1558 (s.), 1447 (m.), 1385 (m.), 1311 (s). 1070 (m.w.), 880 (m.w.) cm^{-1}.

A specimen of (+)-camphor nitrimine had $\lambda_{max}^{C_2H_5OH}$ 2710 Å (ϵ 500) and infrared absorption bands (in chloroform) at 1634, 1558, 1445, 1387, 1311, and 1068 $cm.^{-1}$)

Decomposition of 3-nitriminofriedelane. Water (5 cc.) was added to a solution of the nitrimine (90 mg.) in dioxane (20 cc.) and the mixture heated under reflux overnight. On cooling, there separated a product (70 mg., m.p. 252–258°) which after one crystallization from ethyl acetate gave friedelin as small needles, m.p. and mixed m.p. 255–262°.

Isolation of friedelin from cork resin. The cork resin was placed in a Soxhlet extraction thimble, extracted with ethanol to remove much of the dark-colored impurities which were discarded, then extracted exhaustively with chloroform. Evaporation of the chloroform gave a brown solid (22 g.) which was dissolved in pyridine (375 cc.), to which a solution of hydroxylamine hydrochloride (24 g.) in water (35 cc.) was added, and the mixture heated under reflux for 1 hr. The crude product (18 g., m.p. 250–270° with considerable sintering from 80°), which separated on cooling, was crystallized once from chloroform to give friedelin oxime (9 g., m.p. 273–275°) in purity satisfactory for further processing. Treatment of the oxime (20 g.) with 5% sodium nitrite solution (1000 cc.) in benzene (1000 cc.) and acetic acid (1000 cc.) gave nitriminofriedelane (16.2 g., m.p. 220–221°) which was dissolved in dioxane (2500 cc.)–water (500 cc.), and refluxed for 24 hr. Friedelin (13.1 g., m.p. 255–262°) separated on concentration of the solution.

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

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In previous papers[1,2] we reported the isolation of two new lupine alkaloids, jamaidine $C_{15}H_{24}N_2O_2$ and jamaicensine $C_{14}H_{22}N_2O$, from the seeds of the Papilionaceous trees, *Ormosia jamaicensis* and *Ormosia panamensis*.

That jamaidine is a hydroxylupanine was shown by dehydration with phosphorus pentoxide followed by hydrogenation to produce (+)-lupanine. Catalytic hydrogenation of jamaidine in hydrochloric acid with Adams' catalyst gave desoxyjamaidine, m.p. 178–179°, an isomer of hydroxysparteine. The position of the hydroxyl group had not been determined.

A modified Oppenauer oxidation of desoxyjamaidine has now yielded a ketone identical (infrared spectrum, oxime) with that obtained by oxidation of 13-hydroxysparteine.[3] Therefore desoxyjamaidine must be 13-epihydroxysparteine and jamaidine is 13-epihydroxylupanine I.

Recently, in his paper on the structure of baptifoline, Bohlmann[4] reported the epimerization of

(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.*, **25**, 1959 (1960).

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

13-hydroxysparteine through its tosylate, conversion to the acetate and subsequent hydrolysis. The published infrared spectrum of this 13-epihydroxysparteine was very similar to that of desoxyjamaidine. However, since the melting point (163–164°) of that compound was so much lower than that of desoxyjamaidine, the epimerization was reinvestigated and an authentic sample of 13-epihydroxysparteine was obtained. It proved to be identical in all properties (m.p., infrared spectrum, picrate) to desoxyjamaidine.

Jamaidine is therefore the epimer of the naturally occurring 13-hydroxylupanine and from the work of Bohlmann[4] on the stereochemistry of hydroxylupanine it follows that the hydroxyl group of jamaidine is in the axial position considering ring D in the chair form.

Jamaicensine had been shown[2] to possess a lactam function (α-piperidone), a secondary amino group and a side chain with a terminal vinyl group. No other unsaturation was found in the molecule. Its molecular formula $C_{14}H_{22}N_2O$, as well as its properties, fitted a tetrahydrocytisine structure with an allyl side chain. A possible position for this group, according to biogenetic considerations, is on C-11 next to the secondary amino group.

Since jamaicensine and jamaidine differ only in their molecular formula by one equivalent of formaldehyde it seemed reasonable that jamaicensine could be the precursor of jamaidine. This assumption proved correct and jamaidine was obtained from jamaicensine by a biogenetic-type reaction. A mixture of jamaicensine hydrochloride and aqueous formaldehyde at *p*H 6.5 yielded 51% of jamaidine (13-epihydroxylupanine) after standing three days at room temperature.[5,6] The course of the reaction was followed directly by paper chromatographic examination of the mixture from time to time. At the end of three days pure jamaidine was isolated together with a mixture of unchanged jamaicensine and small amounts of two other unidentified bases. The results in Table I show that a substantial amount of jamaidine is already present after only three hours of standing and that after two days most of the jamaicensine has disappeared. No hydroxylupanine could be detected in the infrared spectrum of the total reaction mixture.

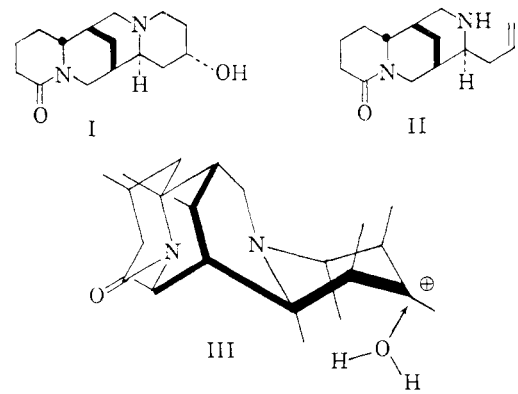
This interrelationship between jamaicensine and jamaidine establishes the structure and the stereochemistry of jamaicensine II.

TABLE I

PAPER CHROMATOGRAPHY[a] OF REACTION MIXTURE

Time, Hr.	R_f and Intensity of Spots
3	0.58 (medium), 0.82 (strong)
28	0.59 (strong), 0.75 (medium), 0.82 (medium), 0.90 (faint)
50	0.58 (very strong), 0.75 (medium), 0.82(f aint), 0.90 (faint)
72	0.58 (very strong), 0.75 (medium), 0.83 (v. faint), 0.92 (faint)

[a] In this system (*sec*-butyl alcohol, hydrochloric acid, water, 100:20:36) jamaicensine and jamaidine had R_f values of 0.82 and 0.58, respectively.



The apparently exclusive formation of jamaidine (13-epihydroxylupanine) is consistent with the mechanism[6] of the reaction involving the carbonium ion III. An examination of spatial models shows that in the final step, the attack on the carbonium ion by water is more likely to occur on the less hindered side of the molecule and would give rise to a hydroxyl group in the axial position. It is conceivable that under other conditions both epimers could be obtained.

EXPERIMENTAL[7]

Modified Oppenauer oxidation of desoxyjamaidine. To a dried powder of potassium *t*-butoxide prepared from 0.2 g. of potassium and an excess of *t*-butyl alcohol was added 10 ml. of dry thiophene-free benzene and 0.35 g. of fluorenone. The mixture was cooled to 5–10° under a nitrogen atmosphere and a solution of 0.2 g. of desoxyjamaidine in 15 ml. of dry benzene was added while the mixture was stirred. The pale yellow mixture turned brown almost immediately. It was stirred at 10° for 30 min., then at room temperature for another 30 min. The benzene solution was extracted with three portions of 1*N* hydrochloric acid. The aqueous extract was washed with ether, then made strongly alkaline with solid potassium hydroxide and extracted with chloroform until it no longer gave a positive alkaloid test. The chloroform solution was dried and evaporated. It yielded a thick

(4) F. Bohlmann, E. Winterfeldt, and H. Brackel, *Ber.*, 91, 2194 (1958).

(5) This experiment was modeled after Grewe's preparation of 10-hydroxydecahydroisoquinoline from cyclohexenyl ethylamine hydrochloride and formaldehyde. R. Grewe, R. Hamann, G. Jacobsen, E. Nolte, and K. Riecke, *Ann.*, 581, 85 (1953).

(6) Several other reactions of this type where the olefin, amine and aldehyde are three separate components, have been described in the literature. (a) G. F. Hennion, C. C. Price, and V. C. Wolff, Jr., *J. Am. Chem. Soc.*, **77**, 4633 (1955). (b) C. J. Schmidle and R. C. Mansfield, *J. Am. Chem. Soc.*, **77**, 4636, 5698 (1955); **78**, 425, 1702 (1956).

(7) All melting points were observed on a Kofler hot-stage. The infrared spectra were recorded on a Beckman IR-7 double beam spectrophotometer in chloroform solution. Analyses were performed by Mr. J. F. Alicino, Metuchen, N. J.

yellow oil which upon evaporative distillation afforded 160 mg. (80%) of colorless oil. Its infrared spectrum showed a strong ketone absorption band at 1720 cm.$^{-1}$ An oxime was prepared and recrystallized three times from ethanol to give small prisms, m.p. 234–236° dec.

Anal. Calcd. for $C_{15}H_{25}ON_3$: C, 68.40; H, 9.57; N, 15.96. Found: C, 68.67; H, 9.49; N, 15.89.

NOTE ADDED IN PROOF: Since this work was submitted two papers dealing with the structure of angustifoline have appeared. L. Marion, M. Wiewiorowski, and M. D. Bratek [*Tetrahedron, Letters*, No. 19, 1 (1960)] and F. Bohlmann and E. Winterfeldt [*Ber.*, **93**, 1956 (1960)] independently reinvestigated the chemistry of angustifoline. In distinction to the earlier work [M. Wiewiorowski, F. Galinovsky, and M. D. Bratek, *Monatsh.*, **88**, 663 (1957)], angustifoline was found to contain a secondary amino group, and our earlier observation[2] that jamaicensine and angustifoline were probably identical has been confirmed. Both groups arrived at the same structural proposal by converting angustifoline to epihydroxylupanine by formaldehyde addition. It is interesting to note that the chemical addition of formaldehyde to jamaicensine leads to jamaidine, and that both occur in *O. jamaicensis* seeds, while the 13-hydroxy epimer, hydroxylupanine, occurs in *Lupinus* species.

Modified Oppenauer oxidation of 13-hydroxysparteine. The oxidation of 0.2 g. of 13-hydroxysparteine (prepared by reduction of 13-hydroxylupanine) was run in the same manner as that of desoxyjamaidine. It yielded 0.18 g. (90%) of thick colorless oil. The infrared spectrum was identical to that of the preceding ketone. An oxime was also prepared, m.p. 234–236° dec.[8] It gave no depression in a mixed melting point with the oxime prepared from the oxidation product of desoxyjamaidine.

Epimerization of 13-hydroxysparteine. The epimerization was carried out essentially by Bohlmann's[4] method. Colorless needles, m.p. 178–179°, were obtained. A mixed melting point with desoxyjamaidine showed no depression. The infrared spectrum of this 13-epihydroxysparteine was identical in all respects to that of desoxyjamaidine. A picrate was also prepared and recrystallized from ethanol, m.p. and mixed m.p. with desoxyjamaidine dipicrate 122° dec.

Conversion of jamaicensine to jamaidine. A solution of 140 mg. of jamaicensine hydrochloride, 100 mg. of aqueous formaldehyde solution (36%), and 0.5 ml. of water was allowed to stand stoppered at room temperature. The *p*H of the solution was approximately 6.5. The course of the reaction was followed by paper chromatography. From time to time a drop of the reaction mixture was chromatographed on Whatman #1 paper in a solvent system of *sec*-butyl alcohol, hydrochloric acid, and water (100:20:36). The results are given in Table I in the text.

After 3 days the solution was made strongly basic with 50% sodium hydroxide and exhaustively extracted with chloroform. The extract dried and evaporated *in vacuo* yielded 121 mg. of pale yellow oil. Upon addition of ether crystalline material separated. It was recrystallized once from acetone to yield 69 mg. (51%) of colorless needles, m.p. 194–195°. The melting point was not depressed on admixture with jamaidine. The infrared spectrum was identical to that of jamaidine. The noncrystalline residue (45 mg.) examined by paper chromatography appeared to be a mixture of four products: two compounds of R_f 0.58 (jamaidine) and 0.75 in approximately equal amounts, and traces of material of R_f 0.82 (jamaicensine) and 0.90. This residue was chromatographed on alumina in an attempt to isolate the compound of R_f 0.75. No separation was accomplished. The compound was either retained on the column or it decomposed and only a small amount of impure jamaidine was recovered.

(8) Galinovsky[3] reports a melting point of 244–245° for this oxime.

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Methyl 2-Deoxy-2-sulfoamino-β-D-glucopyranoside Trisulfate and the Preparation of Tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranosyl Bromide[1]

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A knowledge of the fundamental chemistry of derivatives of 2-amino-2-deoxy-D-glucose (D-glucosamine) containing both sulfoamino and ester acid sulfate groups is important for the proper understanding of the chemical nature of heparin and related polysaccharides. Meyer and Schwarz[3] reported the preparation of the amorphous 2-deoxy-2-sulfoamino-D-glucose (ammonium salt) and its instability toward acid hydrolysis. Wolfrom and McNeely[4] investigated the inactivation of heparin by mild acidity and reported a loss of only 8% of the total sulfur content. This low value of sulfate release is now believed to be due to the peptization sequestration of the barium sulfate by the intact heparin molecule. Jorpes and associates[5] reported that on subjecting alkali-treated heparin to hydrolysis in very dilute hydrochloric acid, exactly equivalent amounts of sulfate and amino nitrogen were released.

We report herein the details of our preparation of an amorphous barium salt of methyl 2-deoxy-2-sulfoamino - β - D - glucopyranoside trisulfate dihydrate by the sulfation of methyl 2-amino-2-deoxy-β-D-glucopyranoside hydrochloride with chlorosulfonic acid and pyridine. The glycoside used was made by the reaction of tri-*O*-acetyl-2-amino-2-deoxy-α-D-glucopyranosyl bromide hydrobromide with methanol and subsequent deacetylation. The glycosyl halide was first prepared by

(1) Preliminary communication: *J. Am. Chem. Soc.*, **75**, 1519 (1953).

(2) Fellow of the Bristol Laboratories, Inc., Syracuse, N. Y.; The Ohio State University Research Foundation Project 432.

(3) K. H. Meyer and D. E. Schwarz, *Helv. Chim. Acta*, **33**, 1651 (1950).

(4) M. L. Wolfrom and W. H. McNeely, *J. Am. Chem. Soc.*, **67**, 748 (1945).

(5) J. E. Jorpes, H. Boström, and V. Mutt, *J. Biol. Chem.*, **183**, 607 (1950).