1,3-Dibromo-2,4-dihydroxy-2(or 3)-methylbutane (XIV). To a stirred solution of 20.0 g. (0.29 mole) of isoprene (XIII) in 250 ml. of water was added 106 g. (0.59 mole) of *N*-bromosuccinimide in portions over 2 hr., maintaining the temperature at 15–20° with the aid of an ice bath. After the addition was complete, the reaction mixture was allowed to stand at room temperature overnight, then was extracted with three 100-ml. portions of ether. The combined extracts were washed with 100 ml. of water, dried over magnesium sulfate, then evaporated to dryness *in vacuo* to give a sirup which crystallized on standing. This crude product was dissolved in 60 ml. of ether and diluted with 100 ml. of petroleum ether (b.p. 30–60°). The solution was concentrated *in vacuo* to approximately 40 ml. at 0°, at which point crystallization occurred to give 21.0 g. (27%) of crystalline dibromohydrin (XIV), m.p. 81–83°; $\lambda_{max(\mu)}^{Nujol}$ 3.0 (OH), 9.35, 9.78 (C—OH), no C=C at 6.1–6.2 or C=CH_2 at 10.1.

Anal. Calcd. for $C_5H_{10}Br_2O_2$: C, 22.9; H, 3.81; Br, 61.1. Found: C, 23.0; H, 3.94; Br, 61.1.

Evaporation of the mother liquors gave 30 g. (39%) of the stereoisomeric XIV as a sirup; $\lambda_{max(\mu)}^{film}$ 3.00 (OH), 9.35, 9.75 (C—OH).

Anal. Calcd. for $C_5H_{10}Br_2O_2$: C, 22.9; H, 3.81; Br, 61.1. Found: C, 23.7; H, 4.02; Br, 62.4.

Neither the crystalline dibromohydrin nor the mother liquors consumed any periodate over 20 hr. Petrov[7] has recorded m.p. 81–83° for the crystalline isomer of XIV.

On a large scale, 197 g. of isoprene (XIII) gave 199 g. (26%) of crystalline dibromohydrin (XIV), m.p. 80–84°.

1,2:3,4-Diepoxy-2-methylbutane (XV). A solution of 31.4 g. (0.52 mole) of potassium hydroxide in 17 ml. of water was added dropwise to a vigorously stirred suspension of 78.1 g. (0.3 mole) of crystalline 1,3-dibromo-2,4-dihydroxy-2(or 3)-methylbutane (XIV) in 200 ml. of ether. After the addition was complete (about 10 min.), the mixture was stirred for 1.5 hr., by which time solution of the dibromohydrin was complete. The ether layer was separated, then dried over potassium hydroxide and potassium carbonate. The filtered solution was concentrated to 80 ml. at 0° and 22 mm. The residue was distilled through a small Vigreux column to give 6.60 g. (22%) of the colorless diepoxide, b.p. 75–77° (70 mm.); n_D^{25} 1.4279; $\lambda_{max(\mu)}^{film}$ 3.29, 6.75 (epoxide CH), 8.01, 8.10 (C—O—C). This material was 96% pure as shown by vapor phase chromatography.[11]

Everett and Kon[13] obtained a 20% yield of diepoxide, b.p. 55° (20 mm.), when isoprene was allowed to react with perbenzoic acid at 0° for 14 days.

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Friedelin and Related Compounds. IV.[1] A Convenient Isolation of Friedelin

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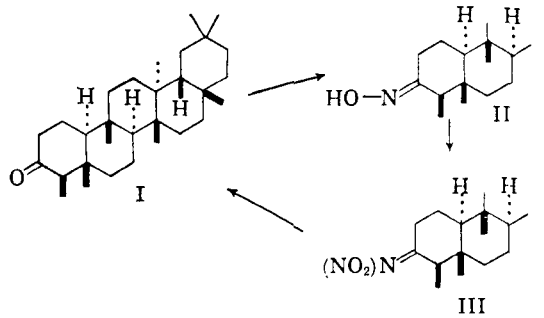
The isolation[2–4] of the pentacyclic triterpene ketone, friedelin (I), in appreciable quantities from cork suffers from the disadvantage of requiring extraction with large volumes of solvent in pilot-plant scale apparatus. A more convenient source, previously utilized,[1,5] is a resin known as "smoker wash solids" obtained as a by-product in the manufacture of corkboard by steam-baking. Friedelin is readily obtained in a crude state from this source by solvent extraction; purification by chromatographic or recrystallization procedures has proven troublesome, however, due to the presence of gelatinous contaminants.

In connection with other studies, friedelin oxime (II) was prepared as described by Drake and Shrader.[6] The realization that this derivative was sparingly soluble in the common organic solvents, notably chloroform in which most triterpenoid compounds are readily soluble, suggested a convenient purification procedure. Preliminary experiments showed that treatment of friedelin with hydroxylamine hydrochloride in aqueous pyridine yielded the oxime in high yield more conveniently. When applied to the neutral crude extract from the cork resin, this method afforded oxime of satisfactory purity after one crystallization from chloroform.

The regeneration of friedelin, in unspecified yield, from the oxime by hydrolysis with phosphoric acid in *n*-amyl alcohol, has previously been reported.[6] In seeking an alternative method, the action of nitrous acid was examined. The effective use of this reagent in hydrolyzing steroid oximes and semicarbazones has recently been demonstrated by Brooks *et al.*[7] who summarize much of the earlier work. Friedelin oxime, on treatment with this reagent, readily gave a product (III), $C_{30}H_{50}O_2N_2$, which in addition to having strong infrared absorption bands (in chloroform solution) at 6.42 and 7.63 μ, characteristic of the nitrimine (pernitroso) function, also had medium intensity bands at 6.16, 6.91, 7.22, and 9.35 μ. An authentic



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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

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