tion gave 2.20 g (76%), bp 55–58° (2.5 mm), of a colorless liquid, which was identified as **2-*t*-butylamino-2-methyl-1-propanol** (2).

Anal. Calcd for $C_8H_{19}NO$: C, 66.15; H, 13.19; N, 9.64; mol wt, 145.24. Found: C, 66.48; H, 12.98; N, 9.56; mol wt, 146 (M + 1) by mass spectrometry.

The infrared spectrum (CCl_4) showed 3610 and 3430 (wide) (OH), 2980, 2880 (CH), 1370, 1220 (*t*-butyl), and 1065 (CO stretching of a primary alcohol) cm^{-1}. The nmr spectrum (CCl_4) showed 1.14 (6 H), *gem*-dimethyl; 1.20 (9 H), *t*-butyl; 2.25 (1 H); NH and 3.11 ppm (2 H), methylene next to oxygen. All signals are singlets. The OH proton does not show up directly A **picrate** of 2 had mp 159–160°, unchanged after recrystallization from ethanol–water.

Anal. Calcd for $C_{14}H_{22}N_4O_8$: C, 44.92; H, 5.92; N, 14.97; mol wt, 374.35. Found: C, 45.11; H, 6.18; N, 14.83.

An **acetate** was prepared from a distilled sample of amino alcohol 2 (2.90 g, 20 mmoles) which was dissolved in 20 ml of acetic anhydride, causing an exothermic reaction. After 1 day of storage at room temperature, ice–water (25 ml) and ether (25 ml) were added, the pH was adjusted to 8 with potassium carbonate, and after a thorough shaking the two layers were separated. The organic layer was washed with water, dried over sodium sulfate, and distilled. The major portion (3.04 g, 81%) had bp 50–55° (8 mm) or 111–112° (60 mm). The boiling point at atmospheric pressure was 189–190° with partial decomposition.

Anal. Calcd for $C_{10}H_{21}NO_2$: C, 64.13; H, 11.30; N, 7.48; mol wt, 187.28. Found: C, 63.95; H, 11.26; N, 7.52.

The infrared spectrum (CCl_4) showed no OH and NH bands in the 3600–3100-cm^{-1} region, 2970 (aliphatic CH), 1737 (ester carbonyl), 1375 + 1385 (dimethyl), and 1235 (CO stretching of acetate and *t*-butyl skeletal vibration) cm^{-1}. The lack of NH stretching vibrations, commonly observed in this series, is probably due to the strong steric hindrance of the highly substituted amine group.

A **phenylurethan** was prepared in the following way. To a solution of 1.45 g (10 mmoles) of distilled 2-*t*-butylamino-2-methyl-1-propanol (2) in 10 ml of *n*-pentane was added phenyl isocyanate (1.43 g, 12 mmoles) and the solution was maintained for 3 days at 0°. The crystalline product was collected and washed with cold *n*-pentane. Recrystallization from hot *n*-pentane afforded needles (2.22 g, 84%), mp 95–96°.

Anal. Calcd for $C_{15}H_{24}N_2O_2$: C, 68.15; H, 9.15; N, 10.60; mol wt, 264.37. Found: C, 68.24; H, 8.82; N, 10.54.

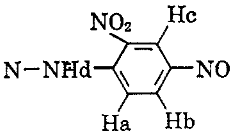
The infrared spectrum (CH_2Cl_2) showed 3400 (NH), 2960 (CH), 1725 (carbonyl of urethan), 1600 (phenyl), and 1525 (amide II) cm^{-1}.

B. Reduction with 0.25 Equiv of Lithium Aluminum Hydride.—To a solution of α-lactam 1 (2.82 g, 20 mmoles) in 30 ml of ether was added 10 ml of a 0.50 *M* solution of lithium aluminum hydride in ether, dropwise, at 0° with stirring. After 30 min of stirring at 0°, water (0.6 ml) was added, and the mixture was stirred for another 0.5 hr. After filtration the inorganic precipitate was washed with ether. The filtrate and washings were evaporated to dryness. To the residual liquid was added a solution of 2,4-dinitrophenylhydrazine (prepared freshly in the following way. 2,4-Dinitrophenylhydrazine (2.0 g, Eastman) was dissolved in 10 ml of concentrated sulfuric acid, then 15 ml of water and 20 ml of alcohol were added. Within 10 min, yellow crystals precipitated. After 12 hr of storage in a refrigerator, the crystals were collected, washed with 95% ethanol, and dried over concentrated sulfuric acid. Recrystallization from hot ethanol–water yielded 1.94 g (23%) of bright yellow crystals, mp 193–194°, characterized as the **2,4-dinitrophenylhydrazone sulfate of aldehyde 3**.

Anal. Calcd for $C_{14}H_{23}N_5O_8S$: C, 39.90; H, 5.50; N, 16.72; S, 7.61; mol wt, 421.42. Found: C, 39.65; H, 5.91; N, 16.68; S, 7.28.

The infrared spectrum (KBr) showed 3275 (NH), 2975, 2810 (CH), 1620, 1590, 1520 (CNO_2), 1335 (CNO_2), 1150, 1080, and 1060 cm^{-1}.

To remove the sulfuric acid from this salt the following procedure was employed. To a suspension of the salt (100 mg) in water (5 ml) and methylene chloride (10 ml) sodium carbonate was added with stirring until pH 9 was reached; the salt dissolved. After thorough shaking the two layers were separated. The aqueous phase was extracted with two 10-ml portions of methylene chloride. The combined methylene chloride extracts were washed with water, dried over sodium sulfate, and evaporated to dryness, leaving an orange, crystalline residue, 70 mg, mp 125–125.5°. The infrared spectrum (CH_2Cl_2) showed 3290 (NH), 2960 (CH), 1620, 1595, 1520 (CNO_2), 1340 (CNO_2), 1225 (*t*-butyl), 1150, and 1080 cm^{-1}. The nmr spectrum ($CDCl_3$) showed 1.18 (9 H), *t*-butyl; 1.43 (6 H), *gem*-dimethyl; 1.7-1.8 (1 H), NH-*t*-butyl; 7.54 (1 H), CH=N; 7.91 (H_a) doublet, J = 9.5 cps; 8.31 (H_b), two doublets, J_1 = 9.5 cps, J_2 = 2.5 cps; 9.10 (H_c), doublet, J = 2.5 cps, and 11.0 ppm (H_d).



The signals at lower field represent the standard pattern for 2,4-dinitrophenylhydrazones.

1-*t*-Butylamino-2-methyl-2-propanol (5).—The starting material, 1,2-epoxy-2-methylpropane, was prepared[3] from 1-chloro-2-methyl-2-propanol (Chemical Intermediates and Research Laboratories sample) in 91% yield, bp 50–52°, $n^{25}D$ 1.3690. A general procedure was followed[4b] for the opening of the epoxide ring with *t*-butylamine. To a 70% aqueous *t*-butylamine solution (36.5 g, 0.5 mole of *t*-butylamine and 15.7 ml of water) was added 1,2-epoxy-2-methylpropane (6.29 g, 0.10 mole) during the period of 1 hr. The solution was refluxed for 1 hr (oil-bath temperature 120°) and then fractionated, to give 11.5 g (79.3%) of 5, bp 103–105° (100 mm) or 45° (3 mm), mp 21–23°, $n^{25.5}D$ 1.4240.

Anal. Calcd for $C_8H_{19}NO$: C, 66.15; H, 13.19; N, 9.64; mol wt, 145.24. Found: C, 66.26; H, 13.00; N, 9.35.

The infrared spectrum (CCl_4) showed 3600 (unassociated OH), 3450 (wide band, associated OH, possibly covering the NH band), 2850–3000 (aliphatic CH), 1375 + 1395 (dimethyl group), 1225 + 1245 (*t*-butyl group), and 1175 (CO stretching of a tertiary alcohol) cm^{-1}. The nmr spectrum ($CDCl_3$) showed 1.10 (9 H), *t*-butyl; 1.16 (6 H), *gem*-dimethyl; 2.47 (2 H), methylene next to nitrogen and 3.64 ppm (1 H), a broad signal, probably NH. All signals are singlets. The OH proton does not show up directly; its presence, however, can be concluded from the integration; the combined signals at 1.20–1.10 ppm integrate for 16 protons, possibly containing the OH proton. The **picrate** had mp 210–211°.

Anal. Calcd for $C_{14}H_{22}N_4O_8$ (picrate): C, 44.92; H, 5.92; N, 14.97; mol wt, 374.35. Found: C, 45.17; H, 6.01; N, 15.07.

The Isolation of Dehydroabietic Acid from Disproportionated Rosin

NOAH J. HALBROOK AND RAY V. LAWRENCE

Naval Stores Laboratory,[1] Olustee, Florida

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The disproportionation of the acids of rosin, in the presence of catalytic quantities of palladium, to a mixture of dehydro- and dihydroabietic acids is a well-known reaction.[2,3] However, the methods for isolating pure dehydroabietic acid from this mixture have been quite tedious, involving its conversion to some derivative, recrystallization of the derivative, and then the regeneration of the acid from the derivative.[2,4–6]

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The method for obtaining pure dehydroabietic acid described in this paper is based on the selective precipitation of the 2-aminoethanol salt of dehydroabietic acid from disproportionated rosin in aqueous alcohol solution. Rosins disproportionated in the laboratory gave amine salt precipitates containing up to 89% of the dehydroabietic acid present in 98% purity.

During the preparation of disproportionated rosin it was observed that the composition of the product dipended on the amount of catalyst as well as the temperature.[2] The dihydroabietic acids first formed were isomerized on further heating. The isomerized acids were much easier to separate from the dehydroabietic acid than were the acids formed under milder conditions. The best starting material for the isolation of dehydroabietic acid was obtained by heating gum rosin with 0.2% of 5% palladium-on-carbon catalyst for 1 hr at 280°.

Four samples were selected to show the applicability of the method. Two were prepared in the laboratory using gum rosin and palladium and two were disproportionated rosins from commercial sources; one from steam-distilled wood rosin (Hercules 731-S) and one from tall oil rosin (Arizona DR-20). The laboratory preparations gave pure dehydroabietic acids after two recrystallizations of the amine salt. The commercial preparations required three to five recrystallizations of the amine salt to give the pure acid. These additional crystallizations of the commercial samples were necessary because they contained a larger amount of the dihydroabietic acid with a relative retention time of 0.80 (Table I) which tends to coprecipitate with the amine salt of dehydroabietic acid.

TABLE I

ANALYSIS OF METHYL ESTERS OF DISPROPORTIONATED ROSINS BY GAS CHROMATOGRAPHY

Relative retention time (methyl dehydroabietate = 1)	Total acids in each peak, %			
	Lab prepn		Comm prepn	
	I	II	III	IV
0.30	1.7	2.3	1.8	1.8
0.64	25.4	17.8	4.6	12.8
0.70	0.5	1.0	<0.1	<0.1
0.75	0.2	1.3	7.2	6.3
0.80	0.4	2.9	10.9	13.8
0.88	0.5	1.0	<0.1	<0.1
1.00	71.3	73.8	75.5	65.3

The difficult-to-separate dihydro resin acid (relative retention time 0.80) was isomerized on continued heating in the presence of palladium–carbon to the dihydro acid with a relative retention time of 0.64. The 2-aminoethanol salt of this isomerized acid was not coprecipitated along with the salt of dehydroabietic acid. The disproportionated rosins contain from 12 to 20% nonacid material. Since these oils are not soluble in the aqueous alcohol solutions they were removed from the amine salt solutions by extraction with isooctane.

Dehydroabietic acid in lower yields was also isolated by this method from two other commercially available rosins which had been disproportionated in the presence of sulfur or sulfur derivative. These rosins were more heterogenous than the palladium-catalyzed diproportionated rosins. The gas chromatography curves obtained on these products were not directly comparable with the products obtained using a palladium catalyst.

Experimental Section[7]

Rosin Disproportionated at 280° with 0.2% of 5% Palladium on Carbon. Preparation I.—WW gum rosin (500 g, acid no. 166) and 1.0 g of 5% palladium on carbon[8] was charged to a flask blanketed with nitrogen and heated rapidly to 280°. The charge was held at 280° with stirring under a slow current of nitrogen (50 ml/min) for 1 hr. The product had acid no. 150. Analysis of the methyl esters by gas chromatography (Table I) showed 98.4% of the acidic portion to be composed of three acids; 71.3% (57% by weight of rosin) of the acids was dehydroabietic acid.

Isolation of 2-Aminoethanol Salt of Dehydroabietic from Preparation I.—A solution of 100 g of the resin in 250 ml of alcohol was filtered through a 0.25-in. pad of Filter Aid. The solution was warmed to 70° and 18 g of 2-aminoethanol (mole/-mole ratio plus 10% based on the acid number of the disproportionated rosin) was added, followed by 250 ml of water at 70–80°. The hot solution was extracted with three 75-ml portions of isooctane. The solution was heated between extractions as necessary to keep the temperature above 60°. Crystallization of the amine salt commences at about 50°.

The solution was refrigerated and the crystals were collected, slurried in 250 ml of cold 50% alcohol, and again collected. Excess solvent was removed by pulling a vacuum on the crystals under pressure of a rubber dam, yield 51.0 g (yield 89.5% of the available dehydroabietic acid), neut equiv 301.5, purity by gas chromatography 98.5%. The salt was crystallized twice from alcohol, after which, gas chromatography of the methyl ester showed only one peak.

The amine salt was dissolved in 160 ml of hot alcohol and acidified to pH 4–5 with dilute hydrochloric acid, and 10 ml of water was added after crystallization had started. The acid was collected, washed with hot water, and recrystallized from 75% alcohol. Drying at 110° (0.5 mm) for 3 hr gave the analytical sample: yield 36.0 g, $\lambda_{\max}^{\mathrm{EtOH}}$ 268 mμ (ϵ 674) and 276 mμ (ϵ 738), $[\alpha]^{25}\mathrm{D}$ +62.0°, mp 171.5–172.5°, neut equiv 300.1 (calcd neut equiv 300.4).

Rosin Disproportionated at 260° with 0.1% of 5% Palladium on Carbon. Preparation II.—WW gum rosin (970 g, acid No. 166) was disproportionated using 0.97 g of 5% palladium on carbon at 260° for 2 hr. The disproportionation procedure of preparation I was followed. The product had acid no. 154. Analysis of the methyl esters of the rosin, prepared by treating an ethereal solution with diazomethane, showed that 74% of the acids (61% by weight of rosin) was dehydroabietic acid. Each of the seven esters separated by gas chromatography was collected in 2-mm (i.d.) glass collection tubes. Each gave a positive tetranitromethane test.

The procedure for precipitation of the amine salt of preparation I was followed. The precipitate gave 49% of the rosin used by weight as dehydroabietic acid: purity 96.5%, neut equiv 303.1. Two recrystallizations of the amine salt and recovery of the acid gave the pure dehydroabietic acid.

Isolation of Dehydroabietic Acid from Commercial Disproportionated Rosin.—The general procedure of preparation I for precipitation of the amine salt, one crystallization, and recovery of the dehydroabietic acid was followed. Preparation III (Arizona DR-20) gave 36.5% dehydroabietic acid: neut equiv 304, mp 162–165°, purity by gas chromatography 98%.

Preparation IV (Hercules 731-S) gave 40.5% dehydroabietic acid: neut equiv 302.1, mp 163–165°, purity by gas chromatography 98.5%.

Acid Components of Disproportionated Rosins.—Methyl esters of the disproportionated rosins, preparations I, II, III, and IV, were prepared by treating an ethereal solution with diazomethane. The composition of the disproportionated rosins as determined by gas chromatography of their methyl esters is shown in Table I. The nonacid material present in the rosin emerged ahead of the rosin ester and did not interfere with the analysis.

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(7) Gas chromatograms were obtained at 240° using a 0.25 in. × 15 ft 5% Versamide 900 resin on 60–80 mesh Chromosorb W, using helium as a carrier gas at 150 ml/min and an F & M Model 500 gas chromatograph. The retention time of the methyl ester of dehydroabietic acid on the columns used varied from 18 to 21 min. Rotations were determined on 2% solutions in 95% alcohol. Product names are used purely for information and do not constitute an endorsement of those named over any other.

(8) The catalyst should disperse freely in the rosin. Products supplied by Baker and Company, Inc., or Engelhard Industries, Inc., Newark, N. J., were satisfactory.