acid, although not actually identified, may be present in minor amount.

Experimental

Saponification of Guayule Resin.—Four kilograms of crude resin, obtained as a by-product from the acetone deresination of guayule rubber[2] reacted with a solution of 400 g. of sodium hydroxide (25 mole per cent. excess based on sapn. equiv. 498) in 5 liters of water. After two hours stirring at a bath temperature of 95° the emulsion was diluted with water, cooled and extracted twice with low-boiling petroleum ether and three times with diethyl ether. Concentration of the petroleum ether extract *in vacuo* yielded 638 g. of viscous yellow oil from which partheniol and other crystalline terpenes (uncharacterized) were isolated by chromatography (activated alumina) and recrystallization from hexane solutions. On solvent removal the diethyl ether extract yielded 1245 g. of viscous reddish oil, making a total of 1883 g. of unsaponifiable material, whose composition is a subject of future investigation.

The saponified fraction was neutralized with dilute hydrochloric acid to liberate over two liters of thick black oil, which was hot-water washed repeatedly to remove cinnamic acid. The color of the oil was lightened by treatment of a solution in diethyl ether with activated charcoal. The residue oil obtained by filtration and solvent evaporation was dissolved in four gallons of petroleum ether. After two hours standing, the supernatant liquid was decanted from 104 g. of black tar. Considerable color clarification resulted from a charcoal treatment of the decantate which was filtered, solvent evaporated, and the residue redissolved in four gallons of methanol. With several hours standing, 16 g. of an oily non-acidic substance was precipitated. The decantate was again treated with charcoal, filtered and concentrated to yield 1920 g. of pale yellow oil (crude fatty acids).

Fractionation of Fatty Acids by Low Temperature Crystallization.—A 400-g. portion of the crude fatty acids, dissolved in 3.6 kg. of acetone, was subjected to a temperature of −20° for several hours. The supernatant solution was then removed by filter stick from a white waxy precipitate. The latter was redissolved in acetone (10% solution) at room temperature, and the solution again cooled to −20° enabling the saturated fatty acids to precipitate.[9] Following a third recrystallization from a 10% solution in acetone, a crystalline fatty acid fraction of 30 g. was obtained. The original filtrate was then chilled to −40° and (after standing) was filtered to yield an additional 11 g. of saturated acids. This fraction was subjected to several separate recrystallizations at −20°, combined with the main (30 g.) fraction, and the total recrystallized repeatedly from hexane to yield 35 g. of white waxy crystals (palmitic–stearic acid eutectic), m.p. 54–54.5°.

The original filtrate was then cooled slowly through two lower temperature stages, −55 and −75°, causing the deposition of unsaturated acid fractions weighing 134 g. and 91 g. With several low temperature recrystallizations, these two fractions appeared to be similar hence were combined and recrystallized, twice each from acetone and hexane at −60°. A yield of 160 g. of pale yellow oil (linoleic acid) was obtained. An additional 122 g. of linoleic acid (total yield 282 g.) and 50 g. of unsaponifiables were isolated from the combined filtrates.

Identification of α-Linoleic Acid.—In Table I are summarized the evidences for the presence of α-linoleic acid in guayule resin.

The tetrabromide, prepared according to Markley,[9] yielded, on repeated recrystallization from benzene, a small portion of a less soluble hexabromide (62.5% Br), m.p. 183–184°. The melting point of hexabromostearic acid is reported[9] as 185.5–186°. This points to the presence of about 1.4% of linolenic acid in the linoleic acid fraction.

The data characterizing guayule unsaturated acid as linoleic acid (Table I) do not preclude the presence of small amounts of oleic acid, especially in view of the indicated presence of about 1.4% of linolenic acid. The slightly low values reported for density, percentage carbon and particularly iodine number (more than cancelling effects of linolenic acid) suggest the presence of more highly saturated material than linoleic acid.

TABLE I

IDENTIFICATION OF α-LINOLEIC ACID IN GUAYULE RESIN

Property	α-Linoleic acid	Guayule unsaturated acid
M.p., °C.	−6.5[9]	−8.5
Carbon, %	77.09	76.5
Hydrogen, %	11.50	11.4
Density, d^{20}_4	0.9025[10]	0.9036
n^{20}_D	1.4699[11]	1.4704
Mol. wt. (neut. equiv.)	280.4	281
Iodine no. (Hanus)	181	175
Tetrabromide, m.p., °C.	115.5[9]	114–114.5
Bromine, %	53.27	53.22
Hydrogenation	Stearic acid	Stearic acid

Identification of Palmitic and Stearic Acids.—Table II summarizes the evidences for the presence of palmitic and stearic acids in guayule resin.

TABLE II

IDENTIFICATION OF A 72.5:27.5 MOLE PER CENT. EUTECTIC OF PALMITIC AND STEARIC ACIDS IN GUAYULE RESIN

Property	Eutectic	Guayule saturated acids
M.p., °C.	55[8]	54–54.5
Carbon, %	75.23	75.4
Hydrogen, %	12.63	12.7
Mol. wt., (neut. equiv.)	264.1	269
Iodine no. (Hanus)	0.0	1.1

The resolution of this eutectic of palmitic and stearic acids, sometimes confused in the past with margaric acid which is now known to be absent in natural fats and oils, has been accomplished elsewhere[12] by columnar partition chromatography. Our preliminary efforts to separate this binary mixture by differential migration with solvents on paper have engendered some promise. Encouraging results were obtained by employing an ascending micro technique[13] with 80% aqueous acetone as mobile solvent on untreated Whatman No. 1 paper with 1% aqueous potassium permanganate for developer. The use of a stearatochromic chloride[14] or a methyltrichlorosilane[15] treated paper offered doubtful improvement and increased the difficulty of obtaining a satisfactory stain. In no case was complete separation of these two acids realized. However, with each of the eluting solvents tested including 80% aqueous acetone, 90% aqueous methanol and *n*-butanol satd. with ammonia–ammonium carbonate buffer solution, there was a pronounced resemblance of pattern between the known fatty acid eutectic and that isolated from guayule resin. This similarity of chromatographic behavior serves to confirm the other data supporting the identification.

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[9] K. S. Markley, "Fatty Acids," Interscience Publishers, Inc., New York, N. Y., 1947.

[10] "Handbook of Chemistry & Physics," 29th ed., Chemical Rubber Publishing Co., Cleveland, Ohio, 1945.

[11] A. W. Ralston, "Fatty Acids and their Derivatives," John Wiley and Sons, Inc., New York, N. Y., 1948, p. 129.

[12] L. L. Ramsey and W. I. Patterson, *J. Assoc. Offic. Agri. Chemists*, **31**, 441 (1948).

[13] L. B. Rockland and M. S. Dunn, *Science*, **109**, 539 (1949).

[14] D. Kritchevsky and M. Calvin, THIS JOURNAL, **72**, 4330 (1950).

[15] T. F. Banigan, Jr., *Science*, **117**, 249 (1953).

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Some Disubstituted Pyridines Related to 2,6-Lutidine

BY RODERICK A. BARNES AND HENRY M. FALES

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In a recent synthesis of the 3,9-diazabicyclo(3.3.1)nonane ring system[1] several attempts were made

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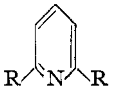
[1] R. A. Barnes and H. M. Fales, THIS JOURNAL, **75**, 975 (1953).

to convert the methyl groups of 2,6-lutidine (I) into substituents which would be suitable for further transformations toward the desired bicyclic system. Oxidation to dipicolinic acid was the only procedure which gave satisfactory yields of a useful intermediate. The transformations described in this report produced interesting substances but the yields were very low.

The dilithium salt of 2,6-lutidine reacted with bromine in ether to form small amounts of 2,6-di-(bromomethyl)-pyridine (II) and large quantities of an acid-soluble brown polymer. The reaction of N-bromosuccinimide with I also produced II along with some 6-bromomethyl-2-methylpyridine (III). Although Buu-Hoi[2] has stated that side-chain brominations in the heterocyclic series proceed easily with N-bromosuccinimide we have been able to obtain II in only 2% yield by this procedure.

When diethyl dipicolinate (IV) was reduced with lithium aluminum hydride a low yield of 2,6-di-(hydroxymethyl)-pyridine (V) was formed. Conversion of this diol to the dibromide II with hydrobromic and sulfuric acids served to confirm the structure of II.



I, R = CH_3
II, R = CH_2Br
IV, R = $COOC_2H_5$
V, R = CH_2OH

Dibromide II, even when analytically pure, melted over a range of 10 to 30° depending on the rate of heating. Melting was accompanied by the formation of a red color which remained after the sample cooled. It is believed that intermolecular quaternization may be taking place as the sample is heated. An attempt to hydrolyze II using silver oxide in aqueous ethanol did not yield diol V but a red substance similar to that obtained by heating II.

Experimental[3]

Diethyl Dipicolinate (IV).—Dipicolinic acid (25.0 g.) prepared by permanganate oxidation of 2,6-lutidine[4] was refluxed with 150 ml. of absolute ethanol while dry hydrogen chloride was introduced in a steady stream. When the acid had completely dissolved the excess ethanol was quickly distilled. The residual oil was then slowly heated on an oil-bath under full aspirator-vacuum until the product abruptly evolved hydrogen chloride.

The acid-free residue was distilled at 158° (1 mm.) to yield 20.0 g. (60%) of a sweet-smelling solid which melted at 41–42°.[5]

Anal. Calcd. for $C_{11}H_{13}NO_4$: C, 59.18; H, 5.87. Found: C, 59.22; H, 5.90.

2,6-Di-(bromomethyl)-pyridine (II). A.—A solution of phenyllithium in ether was prepared from 14.7 g. (2.12 moles) of lithium and 157 g. (1.0 mole) of bromobenzene. Fifty-five ml. (0.51 mole) of 2,6-lutidine was added to the ethereal solution and stirred overnight. To this mixture, cooled to 10°, 160 g. (1 mole) of bromine was rapidly added with vigorous stirring. Filtration from the solids and polymer left a very lachrymatory ethereal solution which was evaporated at room temperature to yield a dark oil. Rapid distillation at 0.5 mm. produced a white solid consisting of the dibrominated base and biphenyl. Four recrystallizations from petroleum ether produced about 750 mg. (1%) of pure 2,6-di-(bromomethyl)-pyridine which melted with decomposition from 66 to 76° or 66 to 99° depending on the rate of heating.

Anal. Calcd. for $C_7H_7NBr_2$: C, 31.73; H, 2.66; Br, 60.32. Found: C, 31.76; H, 2.64; Br, 60.37.

B.—A suspension of 62 g. (0.35 mole) of N-bromosuccinimide in 200 ml. of dry carbon tetrachloride was heated under reflux and illumination with 20 ml. (0.18 mole) of 2,6-lutidine. Boiling was continued for 15 hours while 1.2 g. of benzoyl peroxide was added in 4 portions. The remaining succinimide was filtered and the filtrate washed quickly with cold sodium bisulfite solution and water. Evaporation of the solvent left an oil which was distilled at 0.5 mm. The partially crystallized distillate was chilled, sucked as free as possible from adhering liquors and recrystallized three times from petroleum ether. About 1 g. (2%) of product was obtained which melted from 66 to 92°. A mixture of the dibromide and that prepared in (A) above, melted from 66 to 92° at the same rate of heating.

6-Bromomethyl-2-methylpyridine Picrate.—The adhering liquors from the crude dibromide II were dissolved in diethyl ether and an ethereal solution of picric acid was added until precipitation ceased. The picrate melted at 143° after four recrystallizations from ethanol.

Anal. Calcd. for $C_{13}H_{11}N_4O_7Br$: C, 37.61; H, 2.67; N, 13.49; Br, 19.25. Found: C, 38.18, 38.17; H, 2.90, 2.82; N, 13.50; Br, 19.12.

2,6-Di-(hydroxymethyl)-pyridine (V).—Diethyl dipicolinate (55.7 g., 0.25 mole) was added to a solution of lithium aluminum hydride (0.4 mole) in diethyl ether. An orange-red color developed immediately. The mixture was stirred overnight and water added to decompose the excess hydride. The ethereal layer was separated and evaporated leaving no residue. Carbon dioxide was passed into the aqueous suspension of solids to precipitate the lithium. The resulting suspension retained a yellow-colored substance which was polymeric. Filtration and distillation of the water-phase left a viscous oil (2 g., 5%) which crystallized upon the addition of ethyl acetate. Recrystallization from this solvent and a single sublimation produced the pure diol which melted at 114–118°. The diol was completely soluble in water and insoluble in dry ether.

Anal. Calcd. for $C_7H_9O_2N$: C, 60.41; H, 6.52. Found: C, 60.49; H, 6.43.

The hydrochloride, after being crystallized from methanol and sublimed, melted with decomposition at 153–160°.

Anal. Calcd. for $C_7H_{10}O_2NCl$: C, 47.87; H, 5.74. Found: C, 47.42; H, 5.66.

The diol was converted to the dibromide by the action of hydrobromic and sulfuric acids. After a small sample was boiled with an excess of 48% hydrobromic and concentrated sulfuric acids for 4 hours, the mixture was poured over ice-water, neutralized with dilute sodium hydroxide, and quickly extracted with ether. Removal of the dried solvents left the dibromide, which after recrystallization from petroleum ether melted from 66 to 74° with decomposition. A mixture of this dibromide and that prepared in (A) above melted from 63 to 76°.

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[2] N. P. Buu-Hoi, *Ann.*, **556**, 1 (1944).

[3] Microanalyses were by W. Manser, Zurich, Switzerland. All melting points are corrected and were determined using the Kofler Hot Stage.

[4] G. Black, E. Depp and B. B. Corson, *J. Org. Chem.*, **14**, 17 (1949).

[5] G. Crippa, M. Long and E. de Martini, *Gazz. chim. ital.*, **64**, 83 (1934), reported a m.p. of 28° for this compound. The difference may have been due to the presence of traces of moisture which appear to lower the m.p. markedly.

Studies in the Wagner Rearrangement. VII.[1] The Dehydration of 2-Phenyl-1-acenaphthenol-1-C^{14}

BY WILLIAM A. BONNER AND CLAIR J. COLLINS

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Several isotopic investigations have been reported[2] in which migration ratios for various sub-

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[1] This document is based upon work performed under Contract Number W-7405-eng-26 for the Atomic Energy Commission at the Oak Ridge National Laboratory.

[2] C. J. Collins and B. M. Benjamin, THIS JOURNAL, **75**, 1644 (1953) and previous papers.