$$BrO_3^- + 9I^- + 6H^+ = 3I_3^- + Br^- + 3H_2O,\ \Delta H_7^0 = -132.02 \text{ kcal./mole} \quad (7)$$

Using Bureau of Standards heat data[3] we calculated $\Delta H_f^0 = -18.70$ kcal./mole for BrO_3^-. Similarly from reactions (1) and (6) we obtain

$$BrO_3^- + 8Br^- + 6H^+ = 3Br_3^- + 3H_2O,\ \Delta H_8^0 = -51.93 \text{ kcal./mole} \quad (8)$$

from which we calculate $\Delta H_f^0 = -17.82$ kcal./mole. Combining the average value of ΔH_f^0 (-18.3 kcal./mole) with the entropy of formation,[3] we calculate $\Delta F_f^0 = 2.1$ kcal./mole. The close agreement with Sammet's[2] value may be fortuitous, as may be seen from a careful examination of the iodine and bromine heat data.

The Bureau of Standards value for ΔH_f^0 of I_2(aq) (5.0 kcal./mole) is based on the temperature coefficient of fifty-year old solubility data. We calculate from more extensive and more recent data[15] the value 5.6 kcal./mole (corrected for hydrolysis). For the heat of iodide complexing of iodine (reaction (2)), the following values have been reported in the literature: $\Delta H_2^0 = -4.30,$[16] $-3.87,$[10] -5.10[17] kcal./mole. All of these are based on the temperature coefficients of the equilibrium constant measured in different ways. From the Bureau of Standards heat data[3] one calculates the value -4.03 kcal./mole. It is apparent that the considerable uncertainty in ΔH_f^0 of I_3^- causes three times this uncertainty in ΔH_f^0 for BrO_3^- (see reaction (7)).

In the case of bromine some calorimetric measurements have been made for the heat of solution of Br_2(l) and for ΔH_4. Again, however, the data are old, rather limited, and not obtained at 25°. Calculations from solubility data[17] lead to ambiguous results, so we must say that at least as much uncertainty exists in the Bureau of Standards value for ΔH_f^0 of Br_3^- as does in the I_3^- value, with the correspondng uncertainty existing in ΔH_f^0 for BrO_3^- calculated from equation (8). (Presumably, I^-, Br^- and H_2O heats of formation are accurately enough known so that they will not introduce significant error.)

From this discussion it should therefore be evident that our final calculations of ΔH_f^0 for BrO_3^- from both types of reductions may be uncertain by as much as several kcal./mole. This uncertainty arises at least as much from the uncertainty in the heats of formation of triiodide and tribromide as from our own experimental uncertainties.

VII. Conclusion

We will take as our final values for the heat and free energy of formation of BrO_3^- our calculated averages: $\Delta H_f^0 = -18.3 \pm 2$ kcal./mole and $\Delta F_f^0 = 2.1 \pm 2$ kcal./mole. Additional evidence for these values is provided by Myers[18] who has recently determined ΔF_f^0 to be 2.5 ± 0.3 kcal./mole from kinetic measurements.

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(15) A. Seidell, "Solubilities of Inorganic and Metal Organic Compounds," 3rd edition, D. Van Nostrand Co., Inc., New York, N. Y., 1940.

(16) Calculated by Davies and Gwynne[10] from the data of G. Jones and B. B. Kaplan, THIS JOURNAL, **50**, 1845 (1928).

(17) A. D. Awtry and R. E. Connick, *ibid.*, **73**, 1842 (1952).

(18) O. Myers, private communication.

NOTES

Isolation of Palmitic, Stearic and Linoleic Acids from Guayule Resin[1]

BY THOMAS F. BANIGAN, JR., AND JAMES W. MEEKS

RECEIVED APRIL 4, 1953

In processing guayule, *Parthenium argentatum* Gray, for the isolation of high-quality natural rubber[2] an acetone extract, termed guayule resin, is obtained as a principal by-product. Earlier investigations[3,4] on the composition of this material revealed the presence of parthenyl cinnamate, the ester of a sesqui-terpene tertiary alcohol whose structure was subsequently determined by Haagen-Smit and Fong.[5] A hard "wax-like" compound was also reported[4] and its distribution in the growing shrub determined.[6] The essential oil which constitutes about 3–5% of the resin was shown[7] to contain α-pinene, 60%; dipentene, 9%; cadinene, 8%; and smaller percentages of sesqui-, di-, tri- and higher terpenaceous hydrocarbons and alcohols.

Studies conducted in this Laboratory have now revealed the presence of linoleic, stearic and palmitic acids, and confirmed the presence of cinnamic acid[3,4] in the resin saponifiables. α-Linoleic acid, isolated and purified by solvent extractions and low-temperature crystallizations, has been found to be a major resin component (*ca.* 37%). Palmitic (4%) and stearic acids (1.6%) were isolated as the 72.5:27.5 mole per cent. eutectic, a mixture often encountered[8] when these two acids are obtained from natural sources. Linolenic acid (0.5%) was isolated only as a bromine addition product. Oleic

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(1) From one of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

(2) F. E. Clark, T. F. Banigan, Jr., J. W. Meeks and I. C. Feustel, *Ind. Eng. Chem.*, **45**, 572 (1953).

(3) P. Alexander, *Ber.*, **44**, 2320 (1911).

(4) E. D. Walter, THIS JOURNAL, **66**, 419 (1944).

(5) A. J. Haagen-Smit and C. T. O. Fong, *ibid.*, **70**, 2075 (1948).

(6) T. F. Banigan, Jr., J. W. Meeks and R. W. Planck, *Botanical Gazette*, **113**, 231 (1951).

(7) A. J. Haagen-Smit and R. Siu, THIS JOURNAL, **66**, 2068 (1944).

(8) J. C. Smith, *J. Chem. Soc.*, **625** (1936).

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 parthenìol 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).