Anal. Calcd. for $C_{17}H_{19}O_2N$: C, 75.80; H, 7.11. Found: C, 75.77; H, 7.01.

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Isolation of Betaine from Guayule[1]

By C. W. Murray and E. D. Walter

In the processing of guayule, *Parthenium argentatum* Gray, for the isolation of natural rubber, a large amount of residual plant material is discarded. It is important to determine whether useful products can be found in and recovered from such residues. Also, since guayule is a satisfactory natural rubber for incorporation with synthetic rubber in building tires, knowledge of the composition of the non-rubber constituents of guayule is of great interest. It is possible that these constituents affect the quality of the rubber.

From the water soluble fraction of the leaves and from the defoliated shrub, betaine was isolated as the hydrochloride.[2]

We have isolated betaine from the acetone and benzene insoluble fraction of guayule rubber, thus proving the presence of betaine in the crude pebble-milled rubber. Betaine was also obtained from the product of each step in the extraction of the rubber, such as the dispersion prepared by cutting or comminuting the shrub in water and used for separation of rubber as latex, the solution obtained in parboiling of shrub to remove leaves, and the pebble mill slurry.

Isolation.—The dry, defoliated guayule shrub (2586 g.) was cut in a Ball and Jewell mill, a 1/4-inch screen being used. The material was placed in an 8-gallon container, and four gallons of cold distilled water was added. The mixture was mechanically stirred for about an hour and drained through a coarse filter paper. A second extraction was made with cold distilled water by allowing the mixture to stand overnight. The product was filtered as before, and the filtrate was added to the first. The combined extract was concentrated by passing steam through copper coils immersed in the liquor. After the extract was transferred to a 2-liter beaker, about 100 ml. of concentrated hydrochloric acid was added. A precipitate consisting of organic material and calcium sulfate formed was filtered off. The filtrate was further concentrated, and again precipitated inorganic salts and some humin-like material were filtered off. The residue was washed with warm methanol, the washings being added to the filtrate. The filtrate was clarified several times with Nuchar and was further concentrated until betaine hydrochloride began to crystallize. The mixture was cooled, and the betaine hydrochloride was filtered off, washed with cold absolute ethanol, and recrystallized from 95% ethanol: yield, 12 g. or about 0.4% of betaine hydrochloride.

The above experiment was repeated on 2893 g. (dry wt.) of defoliated shrub with hot instead of cold water; yield, 14 g. or about 0.5% of betaine hydrochloride.

A similar experiment with 1415 g. of dry, cut leaves yielded 13 g. or about 0.9% of betaine hydrochloride.

Optical Properties.—The betaine hydrochloride, crystallized from 95% ethanol, consisted of monoclinic prisms, tabular forms and triangular fragments. The refractive indices (determined in daylight by immersion in organic liquids) were: $n_\alpha = 1.515$, $n_\beta = 1.535$, $n_\gamma = 1.594$, all ± 0.003. In parallel polarized light (crossed nicols) many crystals did not show complete extinction on rotating the stage. These showed the emergence of a well centered optic axis interference figure by conoscopic observation in convergent polarized light (crossed nicols). The optic sign was positive. The double refraction was strong ($n_\gamma - n_\alpha = 0.079$). The extinction was usually parallel or symmetrical, and an occasional section had positive elongation with an extinction angle of about 35°: $2V = 62° 16'$ calcd.; $r > v$ weak. The optical properties of an authentic sample of synthetic betaine hydrochloride agreed in all respects with those of the material isolated from guayule. This comparison served to positively identify the isolated substance.

Anal.[3] Calcd. for $C_5H_{11}O_2N \cdot HCl$: C, 39.09; H, 7.87; N, 9.12; mol. wt., 153.6. Found: C, 39.0; H, 8.24; N, 8.94; equiv. wt. (when titrated with NaOH to phenolphthalein), 155.6.

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(1) Not copyrighted.

(2) A. J. Haagen-Smit and co-workers, at the California Institute of Technology, previously stated, in a private communication, that they obtained betaine as the hydrochloride from alcohol extracts of guayule shrub.

(3) The authors are indebted to Norman L. Kaufman of this Laboratory for analytical results reported.

Bureau of Agricultural and Industrial Chemistry
Agricultural Research Administration
Guayule Emergency Rubber Project of
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Dielectric Constants of Ethylene Dichloride-Benzene Mixtures

By Arthur A. Vernon, Jeffries Wyman[1] and Robert A. Avery[2]

The dielectric constants of ethylene dichloride and of benzene are well known and the dielectric constants of *dilute* solutions of ethylene dichloride in benzene have been measured by Williams,[3] Gross,[4] and Muller.[5] In the course of some recent experimental work it was necessary to determine the dielectric constants of these solutions over the complete range and the results are given below.

Experimental

The benzene, c. p. thiophene-free, was stored for several days over anhydrous calcium chloride and then distilled from anhydrous aluminum oxide. The first fifth and last

Table I

Dielectric Constant of Benzene-Ethylene Dichloride Mixtures at 25°

Mole fraction of benzene	Wave length in meters	Dielectric constant	$\frac{E-1}{E+2}$
1.000	6.800	2.274	0.29815
0.887	7.533	2.791	.3748
.789	8.215	3.318	.4359
.658	8.8825	3.879	.4897
.554	9.786	4.707	.5527
.395	10.969	5.914	.6209
.281	11.881	6.940	.6644
.143	13.115	8.455	.7131
.000	14.522	10.365	.7574

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(1) Department of Biology, Harvard University.

(2) United States Public Health Service, St. Louis, Missouri.

(3) Williams, *Z. physik. chem.*, **A138**, 75 (1928).

(4) Gross, *Physik. Z.*, **32**, 567 (1931).

(5) Muller, *ibid.*, **34**, 689 (1933).

fifth fractions were discarded; the boiling point of the collected material was 80.2° at 760 mm. pressure. The ethylene dichloride, Eastman Kodak Company practical grade, was stored for several days over anhydrous calcium chloride and distilled from anhydrous aluminum oxide. The fraction collected boiled at 83.5° under 768 mm. pressure. Its index of refraction was 1.4422 compared with the "International Critical Tables" value of 1.44225.

The resonance method as described by Wyman[6] was used for all the measurements, which were made at 25°.

The results of the measurements are shown in the table. Since density measurements were not available, it was not possible to calculate the polarization according to the relation

$$P_{12} = \frac{\epsilon - 1}{\epsilon + 2} \frac{(f_1M_1 + f_2M_2)}{\rho}$$

but it is hoped that this can be done at a later date.

The values for the dielectric constants of pure ethylene dichloride and benzene are in reasonable agreement with the values 10.235 and 2.267, respectively, found by Hooper and Kraus[7] at the same temperature. The data at low concentrations are also in good agreement with the previously determined values by Muller,[5] as nearly as can be judged by interpolation.

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[6] Wyman, *Phys. Review*, **35**, 623–634 (1930).

[7] Hooper and Kraus, THIS JOURNAL, **56**, 2265 (1934).

HAYDEN MEMORIAL LABORATORIES
NORTHEASTERN UNIVERSITY
BOSTON, MASSACHUSETTS

RECEIVED MARCH 28, 1945

NEW COMPOUNDS

Ethyl β-Keto-ϵ-phenoxyhexoate and Ethyl β-Keto-ζ-phenoxyheptoate

These β-keto esters have been prepared by carbethoxylation of the appropriate methyl ketones according to the procedure of Wallingford, Homeyer and Jones.[1]

γ-Phenoxypropyl Methyl Ketone.—Methylmagnesium bromide was prepared from 7.3 g. of magnesium and 29 g. of methyl bromide in 200 cc. of ether. The solution was cooled in an ice-bath while 29.3 g. of finely powdered anhydrous cadmium chloride (dried by heating in a stream of dry hydrogen chloride at 400–450° for three hours) was added. After stirring for two hours, 41.5 g. of γ-phenoxybutyryl chloride[2] was added slowly. After the initial reaction had subsided, the mixture was refluxed for two hours, with the separation of some solids. The reaction mixture was again cooled in an ice-bath and was decomposed by the slow addition of 300 cc. of 5% sulfuric acid. The ether layer was separated and the aqueous layer was extracted twice with ether. The ether extracts were dried over anhydrous sodium sulfate and were concentrated on the steam-bath. The product was distilled, and yielded 29 g. (78%) of the ketone boiling at 120–121° at 2 mm. This solidified upon cooling and melted at 48–50° A sample, recrystallized from methanol by cooling in a Dry Ice-bath, melted at 50–51°.

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.27; H, 7.92. Found: C, 74.40; H, 8.07.

The 2,4-dinitrophenylhydrazone, recrystallized from 95% ethanol, melted at 109–110°.

Anal. Calcd. for $C_{17}H_{18}O_5N_4$: N, 15.63. Found: N, 15.35.

Ethyl β-Keto-ϵ-phenoxyhexoate.—In an apparatus of the type described by Wallingford,[1] 2.6 g. of clean sodium was converted into dry sodium ethylate. With the oil-bath temperature at 50°, that of the heated fractionating column at 45°, and the pressure maintained at 130 mm., 70 cc. of diethyl carbonate and 20 g. of γ-phenoxypropyl methyl ketone in 10 cc. of diethyl carbonate were added. The bath was heated to 110° during thirty minutes and maintained there for one and one-half hours. Most of the alcohol which formed distilled during the first hour. The reaction mixture was then cooled and acidified with 125 cc. of 10% acetic acid. It was then extracted with ether and the ether extract was dried with anhydrous sodium sulfate. The diethyl carbonate was distilled at 20 mm. pressure and the residue fractionated at 1 mm. Four grams of forerun distilling between 130–156° and 9.0 g. (32%) distilling at 156–160° was obtained.

The N-phenylpyrazolone was prepared from 100 mg. of the keto ester and 50 mg. of phenylhydrazine by heating for fifteen minutes in 2.5 cc. of 80% ethanol with 0.1 cc. of acetic acid. After recrystallization from 90% ethanol, it melted at 115–117°.

Anal. Calcd. for $C_{18}H_{18}O_2N_2$: N, 9.52. Found: N, 9.30.

The semicarbazone of the keto ester, after three recrystallizations from 50% ethanol, melted at 217–218°.

Anal. Calcd. for $C_{15}H_{21}O_4N_3$: N, 13.66. Found: N, 13.47.

The ethyl β-keto-ϵ-phenoxyhexoate was also prepared by the acylation of ethyl acetoacetate with γ-phenoxybutyryl chloride and hydrolysis of the phenoxybutyryl acetoacetate by shaking with 10% ammonium hydroxide.[3] The yield of the β-keto ester by this method was 5 to 9% and the product was difficult to purify. However, an N-phenylpyrazolone and a semicarbazone identical with those described above were obtained from the product synthesized by this method.

δ-Phenoxybutyl Methyl Ketone.—To 90 g. of sodium dissolved in 2 liters of absolute ethanol was added 520 g. of ethyl acetoacetate. The solution was stirred and heated to boiling and 860 g. of γ-phenoxypropyl bromide[4] was added over a period of two hours. The refluxing was continued for eight hours. The solution was cooled and decanted from the majority of the precipitated sodium bromide and the sodium bromide was washed with alcohol. The alcohol was removed by distillation on a steam-bath. To the crude ethyl α-aceto-δ-phenoxyvalerate, which weighed about 1300 g., was added a solution of 200 g. of sodium hydroxide in 4 liters of water and the mixture was stirred at room temperature for six hours. At the end of this time, about 250 g. of unsaponified oil remained. This layer was discarded and the aqueous layer was acidified by the drop-wise addition of 144 cc. of concentrated sulfuric acid in 300 cc. of water. The addition of the acid and accompanying decarboxylation was completed in two hours. The oily ketone was separated and the aqueous layer was extracted with ether and the ether extract was combined with the ketone. After drying briefly over sodium sulfate, the ether was removed and the ketone was distilled at 125–130° at 2 mm. The yield was 470 g. (61%) which solidified on cooling to 5°. It melted at 10°.

A sample which distilled at 127° at 2 mm. possessed n^{25}_D 1.5071; d^{20}_{20} 1.0164; M_D calcd. 55.67; found 55.95.

Anal. Calcd. for $C_{12}H_{16}O_2$: C, 74.81; H, 8.38. Found: C, 74.80; H, 8.54.

The 2,4-dinitrophenylhydrazone was recrystallized from 95% ethanol and melted at 100–101°.

Anal. Calcd. for $C_{18}H_{20}O_5N_4$: N, 15.05. Found: N, 15.07.

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[1] Wallingford, Homeyer and Jones, THIS JOURNAL, **63**, 2056, 2252 (1941).

[2] Hanford and Adams, *ibid.*, **57**, 921 (1935).

[3] Bouveault and Bongert, *Bull. soc. chim.*, [3] **27**, 1089 (1902).

[4] "Organic Syntheses," Coll. Vol. 1, 2nd ed., John Wiley and Sons, New York, N. Y., 1941, p. 135.