

of the methylene hydrogen atoms of these two compounds is extremely interesting and suggests the possibility of the synthesis of a series of derivatives exactly analogous to the barbiturates. Unfortunately this is not entirely possible. Alkylation of the arylestere and arylamides can be effected in a manner similar to the malonic acid synthesis, but certain differences in the properties of these two compounds defeat efforts to prepare methylenedisulfonic acid derivatives simulating the barbiturates. The alkylesters of methylenedisulfonic acid do not permit efficient alkylation and when treated with alcohol or ammonia they exhibit properties characteristic of the alkylesters of sulfuric acid. It might be stated that this similarity to sulfuric acid should be expected since the alkylmonosulfonic acids possess some of these properties. However, the insolubility of barium methylenedisulfonate and the inability to form alkylesters and amides from methylenedisulfonylchloride are certainly exceptions to the recognized properties of the alkylmonosulfonic acids.

In spite of our many unsuccessful attempts to prepare cyclic ureides of methylenedisulfonic acid we still are not convinced that these compounds cannot be made. It is our opinion that the properties of the dialkyl derivatives of the free acid might approach those of the more characteristic organic compound malonic acid, and permit the preparation of the cyclic ureide. It was this opinion that encouraged us to endeavor to prepare the free dialkylmethylenedisulfonic acids.

SUMMARY.

1. Methylenedisulfonic acid and a number of its derivatives have been prepared and studied.
2. Methods of hydrolyzing dialkylmethylenedisulfonic acid arylestere and amides have been studied.
3. A number of attempts to prepare the cyclic ureide of methylenedisulfonic acid have been made under varying conditions.

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ACORNS OF QUERCUS RUBRA.*

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Remarkably little attention has been paid to the chemical composition of the common acorn, although it can be obtained in almost unlimited quantity. Attempts have been made repeatedly to utilize the kernels as fodder for cattle, swine and poultry but, because of the tannin content, they are apparently disagreeable

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to the animals even after supplementary mixture with other foods. The fixed oil, however, might find some value in pharmacy and as an edible material. The few analyses which have been made on foreign species would certainly indicate that the product could so be used.

The fruits of the red oak seem to offer considerable possibility along this line. They are abundantly produced from trees which are very common in New England and undoubtedly could be collected in large quantities every year.

A lot of about 30 pounds of these was collected in the fall of 1935 from trees which were identified by Professor Youngken, of the Massachusetts College of Pharmacy. About 35 per cent was found to be shell and 65 per cent kernels. Partial analysis of the latter gave: moisture 11.02; protein ($N \times 6.25$) 4.41; starch 28.23; tannin 11.74; ether extract 11.03 per cent. The high content of tannin and low protein probably explain the objections to using the kernels as a food for animals.

The oil was extracted from several pounds of the macerated material by means of ether, which was subsequently distilled off, the last portions being removed by careful aeration. There was thus obtained nearly a liter of light brown product, depositing about 20 Gm. of solid matter which was not further examined. Analysis of the oil gave the following results:

Specific gravity at 25° C.	0.9141	Unsaponifiable residue	0.9
Refraction at 20° C.	1.4725	Iodine number	100.1
Solidifying point	6.2° C.	Hehner value	90.6
Titer test of acids	13.1° C.	Soluble acids	0.2
Saponification number	195.3	Maumene test	49° C.
Acid number	4.5	Reichert-Meißl value	1.1
Ester number	190.8	Polenske value	0.8
Acetyl value	5.3		

Using the common method involving solubility of the lead salts in ether, the liberated acids were separated roughly into a solid and a liquid portion. The isolated solid acids had a melting point of 53° C. and an iodine number of 6.04 and, correcting for the latter, amounted to 9.22 per cent. By exposing a saturated solution in ether to a temperature of -5° C., it was possible to obtain a portion melting at 56.2° C. and having an acid number of 284 and a second portion with 51° C. and 272, respectively. Apparently most of the solid acids consist of stearic acid with smaller amounts of palmitic.

The oil contained mostly liquid acids with an iodine number of 110.3, giving by calculation a total of 76 per cent. Bromination of the product gave rise to no substance insoluble in petroleum ether, acetone or chloroform and no separation could be obtained from the resulting solutions at low temperatures. One can conclude that the liquid acids consist chiefly of oleic and, because of the high iodine value, one of the linoleic acids. Linolenic acids, which give solid hexabromides, must be absent.

We find, therefore, that the fixed oil from acorns of *Quercus rubra* is somewhat similar to that from other species of oak. It is also clearly related to other oils of the semi-drying and non-drying classes, such as olive and cottonseed. The taste of the material is quite agreeable and there seems to be no doubt that it could be employed successfully as emollient in medicine and probably in other ways in which fats are generally applied. We are at present contemplating a more complete study of composition and of methods for collection and refining.

SUMMARY.

1. Analysis was made of the kernels of *Quercus rubra* and of the oil which they contain.
2. The oil consists largely of glycerides of oleic, linoleic, stearic and palmitic acids. It conforms closely to other fatty oils used in medicine.

THE BARK OIL OF DOUGLAS FIR.*

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The bark of the young Douglas fir, *Pseudotsuga taxifolia* (Poir.) Britt., is characterized by the presence of numerous resin blisters which disappear as the tree grows older while the bark becomes thicker and deeply furrowed. It was from this young bark that the oil used in this investigation was obtained.

EXPERIMENTAL.

Pieces of bark were cut from selected trees growing in the vicinity of Seattle, Washington, and subjected to steam distillation. From 64 pounds of fresh bark there was obtained a total of 338 cc. of oil which corresponded to a yield of 1.01 per cent. The oil was slightly greenish in color and possessed a very pleasing aromatic odor.

The physical constants of the oil were determined in the usual manner with the following results: d_{20} 0.8721; n_D^{20} 1.4750; $[\alpha]_D^{23}$ -24.25° ; saponification number 11.9; acid number 0.71; ester number (calculated) 11.19; per cent of ester (calculated as geranyl acetate) 3.9; saponification number, after acetylation 62.4; per cent of total alcohol (calculated as geraniol) 17.5; per cent of free alcohol (calculated as geraniol) 14.4.

Free Acids.—Extraction of 250 cc. of the oil with a 5 per cent aqueous solution of sodium carbonate gave 0.2102 Gm. of a brown gummy residue which was slightly acid to litmus and possessed a faint odor. The residue was dissolved in ether and steam distilled, whereupon an aqueous distillate was obtained on the surface of which floated a small amount of insoluble material. Attempts were made to identify acids present in both the soluble and insoluble distillates but without success. The odor of the distillates as well as their reactions to litmus indicated at least the presence of traces of acids such as capric or caproic.

Phenols.—Extraction by 5 per cent aqueous solution of sodium hydroxide yielded 0.1767 Gm. of a resinous brown residue possessing a faint odor. The residue did not respond to any of the general tests for phenols, hence it was concluded that no phenols were present in the bark oil.

Fractionation.—The oil, which had been extracted with the sodium carbonate and sodium hydroxide solutions, was washed with water and dried. The 238 cc. of oil which remained were fractionated at 25-mm. pressure and that portion boiling up to 100° C. was separated. This lower boiling portion, which measured 184 cc. and represented 73.6 per cent of the original oil, was resolved into its various constituents by repeated refractionations. The fractions as finally obtained, together with their physical constants, are as follows:

Fraction No.	Boiling Point at 25 Mm.	Amount.	Sp. Gr. 20° C.	n_D^{20} .	$[\alpha]_D^{23}$.	Color.
I	65–71° C.	88 cc.	0.8575	1.4751	-35.21°	Colorless
II	71–80	75	0.8586	1.4804	-25.59	Colorless
III	80–100	21	0.8720	1.4866	-11.08	Colorless

Levo Alpha Pinene.—A portion of the first fraction was oxidized to pinonic acid with potassium permanganate according to the method of Tiemann and Semmler (1). The semicarbazone

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