

The fact that present American forest practice looks to the timber crop as almost the sole source of revenue has its disadvantages in spite of being a safe investment. Particularly when the project has to begin with reforestation, it is a long-time investment and that is not overly attractive to capital in a country that is scarcely out of the exploitation stage. Hence it seems desirable to find means of deriving some sort of annual return from forest areas in order to reduce the overhead, even if it should not be possible to pay the interest on the investment.

In order to accomplish this end, other products than mature timber must be found. Up to the present, the so-called forest industries, the naval-stores industry and the wood distillation industry have almost competed with lumbering in wanton destructiveness. The more recent paper pulp industry is said to be more conservative because the installation is much less mobile. But all of them use more or less mature timber. This problem of studying and of developing non-timber forest products has seemed to the author and his students a most interesting source of materials for studies in organic and plant chemistry. The forest as a whole will be studied for whatever chemical products it may yield. The investigations are being carried on in the belief that any and all contributions to scientific fact will ultimately reap their practical benefit when their interrelations have been sufficiently understood. But it is just these interrelations which will be most carefully considered with a view to formulating a sequence of products for each month of the year. And when the desired plants have been sufficiently studied so that they can be grown with as much assurance as any other crop then we shall have a new forest management which will rank as an agricultural-chemical industry.

The easiest approach seems to be through the drug plants about many of which something is already known. It is because of these intimate relations to pharmacognosy and pharmaceutical chemistry that the series of papers, "Contributions to the Knowledge of Forest Products," growing out of the studies in the Vanderbilt Laboratory for Organic Chemistry, will be published for the present in this JOURNAL.

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CONTRIBUTIONS TO THE KNOWLEDGE OF FOREST PRODUCTS.

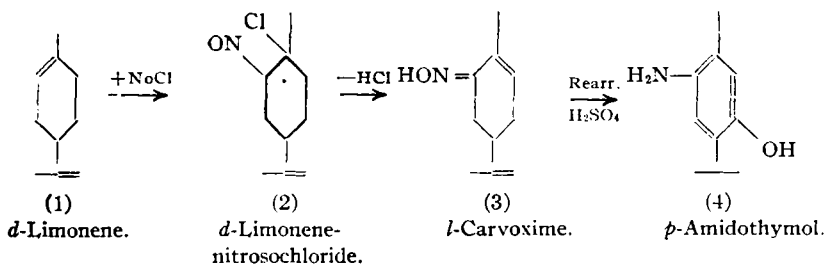
I. THE PREPARATION OF *p*-AMIDO-THYMOL FROM *d*-LIMONENE.*

BY A. C. GRAYBEAL AND R. E. KREMERS.

Limonene is an important constituent of many volatile oils. Although isomeric with pinene and very frequently associated with it, limonene does not have the same importance in the oils of the Coniferae that pinene has. In fact it is, broadly speaking, true that where one predominates the other is recessive, and that pinene characterizes the oil from the oleoresin whereas limonene is more characteristically found in the leaf and twig oils. As the latter are valued for their content of borneol or terpineol or esters of these alcohols, it seemed of interest to consider possible methods for the chemical utilization of the less valuable limonene.

The reactions chosen for study had all been previously recorded separately in the literature.

* Abstracted from a thesis presented by A. C. G. to the Graduate School of Vanderbilt University in partial fulfillment of the requirements for the degree of M.S., June 1921.



Wallach¹ had improved the method for the preparation of limonene-nitrosochloride (2) originally obtained by Tilden.² Goldschmidt and Zuerrer³ proved the identity of the carvoxime (3) obtained from carvone with that from limonene-nitrosochloride. Later Wallach⁴ used carvoxime from carvone and hydroxylamine to prepare *p*-amido-thymol (4). Thus it happened that this compound had never been prepared with limonene as the starting point. That this had not been done is probably due largely to the difficulty often encountered in obtaining a satisfactory yield of the nitrosochloride, which fact may be partly explained by the existence of Deussen's "New Carvoxime."⁵ This investigation was undertaken in order to help clear up this stumbling block and to study more closely certain reactions of *p*-amido-thymol.

PURIFICATION OF LIMONENE.

As a source of *d*-limonene both washed oil of lemon and washed oil of orange were used. The terpene was purified by the usual method of careful fractionation *in vacuo* and final distillation over sodium. The physical constants of the limonene thus obtained were:

- ex. lemon oil,
 B. $p_{.760} = 173-74^\circ \text{C.}$; B. $p_{.21} = 74-76^\circ$; $d_{20} = 0.8410$; $n_{20} = 1.7350$; $a_{23} = +86.126^\circ$.
 ex. orange oil,
 B. $p_{.760} = 173-74^\circ \text{C.}$; B. $p_{.14} = 68-70^\circ$; $d_{26} = 0.8127$; $n_{26} = 1.4693$; $a_{26} = +114.66^\circ$.

PREPARATION OF LIMONENE-NITROSOCHLORIDE.

Limonene-nitrosochloride was prepared from the above samples of terpene. The reaction was first carried out according to Wallach's directions.⁶ To a solution of 5 cc of limonene and 11 cc of ethyl nitrite in 10 cc of glacial acetic acid previously chilled in a freezing mixture, a solution of 5 cc concentrated hydrochloric acid in 5 cc of glacial acetic acid was added drop by drop. When about half the acid had been added the white nitrosochloride began to precipitate out. At the end of the reaction precipitation was completed by the addition of 5 cc of 95 percent alcohol. The nitrosochloride was filtered by suction and washed with alcohol until perfectly white and therefore free from green mother liquor. From three such reactions the average yield was 1.025 Gm.

These conditions were then modified by replacing the acetic acid with alcohol. For two reactions in which alcohol was the only solvent an average yield of 1.48 Gm. was obtained.

Finally the following proportions were used. To a solution of 5 cc of limonene and 11 cc of ethyl nitrite in 10 cc of glacial acetic acid and 10 cc of 95 percent alcohol, 5 cc of concentrated hydrochloric acid were added. By this procedure an average yield of 3.15 Gm. was obtained. When tried on a larger scale, 33.8

Gm. of limonene-nitrosochloride were obtained from 50 cc of limonene, and 72 Gm. from 100 cc of limonene. As is evident, these conditions are favorable for quantity production in the laboratory. To be successful, however, it is necessary to observe the following precautions: The ethyl nitrite should be freshly prepared: mechanical stirring insures proper refrigeration and mixing; and the product must be thoroughly washed with cold 95 percent alcohol until it is glistening white and free from all traces of mother liquor. It is especially necessary to observe this last condition in order to prevent subsequent decomposition if the product is not used immediately.

PREPARATION OF CARVOXIME.

Of the varying conditions employed for the conversion of nitrosochloride into carvoxime, two of the slightly more favorable attempts are herewith described. Five grams of nitrosochloride and 1 gram of potassium hydroxide dissolved in alcohol were mixed in an acetylation flask and cautiously heated until the rather violent reaction was complete. The reaction product was isolated by pouring the alcoholic solution into water and extracting with ether. After evaporation of the solvent a non-crystallizable gum was obtained. The products of several reactions were mixed and distilled at 24 mm. pressure until decomposition set in. The oily distillate now crystallized on standing and the crystals were obtained in a state of purity by recrystallization from 40 percent alcohol.

M. p. found, 73° C.; recorded for *l*-carvoxime, 73° C.

In working with larger quantities, the following procedure was tried: 72 Gm. of nitrosochloride were placed in a flask provided with an adapter that carried both a reflux condenser and a dropping funnel. A portion of alcoholic potassium hydroxide was added at once and the mixture heated on the water-bath. The remainder was added as the reaction progressed as indicated by phenolphthalein. After completion of the reaction, the product was precipitated by water, extracted with ether, and steam-distilled. The residual oil then crystallized almost immediately after it had been separated from the hot water. The carvoxime was recrystallized as before; yield 9.2 Gm.; percent yield 15.7 percent; m. p. 73.5° C.

p-AMIDO-THYMOL.

The carvoxime thus obtained was converted into *p*-amido-thymol by Wallach's method,⁴ the yields being satisfactory.

M. p. found, 173° C.; recorded, 173°.

Wallach reports that *p*-amido-thymol can be diazotized in sulphuric acid solution and coupled with phenols. While the reaction undoubtedly takes place, it does not appear to be altogether free from side reactions which are difficult to control. In spite of repeated attempts, no two reactions yielded products of the same melting point. Hence it seems desirable to leave this problem for a separate report.

SUMMARY.

p-Amido-thymol has been prepared direct from *d*-limonene.

The conditions for the preparation of limonene-nitrosochloride and for its conversion into carvoxime have been more clearly defined.

It has been found that under the usual conditions the diazotization and coupling of *p*-amido-thymol do not proceed smoothly.

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THE INFLUENCE OF METHODS OF DISTILLATION ON THE COMMERCIAL VALUE OF OIL OF AMERICAN WORMSEED.

BY G. A. RUSSELL.

INTRODUCTION.

Within the past few years considerable difficulty has been experienced by the trade in securing wormseed oil that conforms to the U. S. P. specifications. Whereas small lots of oil have been secured in quantities to meet the spot demand to a greater or less degree, the supply left in the hands of the producers has been of relatively large magnitude. This oil was probably, without exception, of such character that it did not test up to the U. S. P. requirements, and this condition of affairs appears to have grown more and more acute until at the present time it is stated that more than 50 percent of the crop is still in the hands of the producers.

Such a condition would naturally point to three possible explanations: (a) adulteration, (b) a change in the character of the oil brought about by long and intensive cultivation and selection of the plants, or (c) a change in the method of distillation at the distilling plants.

It is believed that no instances of adulteration have been disclosed by the offices charged with the enforcement of the Food and Drugs Act, and thus the first supposition is at once eliminated. While it is perhaps true that long and intensive cultivation, accompanied by seed selection, or type selection, would influence the character of the oil to some extent, to prove this would require study over a period of years, and there is no evidence that such a study has been made. There remains, then, the third supposition that the method of distillation at the distilling plants might produce changes in the oil which would cause it to be rejected as not up to specifications.

In 1908 Schimmel and Company¹ pointed out that the distillation of *Chenopodium* herb must be accomplished by the exercise of certain precautions in order that an oil might be secured which would conform to the standards of that time. Later Nelson² laid emphasis on the method of distillation, stating, ". the valuable and chief ingredient, is unstable, and is decomposed gradually on boiling with water. Consequently, the distillation must be carried on rapidly with steam at a good pressure, the condenser kept warm and the warm distillation water separating from the oil in the receiver, discarded."

The second precaution mentioned by Nelson has no effect on the composition of the oil but does tend to effect a better separation of the oil in the receiver. The densities of warm water and warm wormseed oil vary by a greater degree than do

¹ Schimmel and Company, "Semi-Annual Report," April 1908, p. 109.

² E. K. Nelson, "The Composition of Oil of *Chenopodium* from Various Sources," *J. Am. Chem. Soc.*, 42, 1204, 1920.