Naval Stores Research at the Forest Products Laboratory, Past and Present

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As many of you may not be familiar with Forest Products Laboratory, allow me to introduce it to you. The Forest Products Laboratory is a Federal government laboratory of the United States Department of Agriculture and, more specifically, of the Forest Service. The Laboratory was built in Madison, Wisconsin in close cooperation with the University of Wisconsin to serve as-the national center for wood utilization research.

The broad mission of Forest Products Laboratory is "to improve utilization of wood through research that leads to improved management of the timber resource, thus meeting the needs of the United States and contributing to the international community." Utilization research at the Laboratory covers eleven program areas:

Program Area	Number of Scientists and Other Technical Professionals
Material Properties and Construction	18
Pulp and Paper	17
Preservation and Protection	13
Composite Products and Adhesives	12
Biological Conversion Processes	9
Timber Requirements and Economics	9
Solid Wood Processing	8
Mycology	5
Chemicals and Energy	4
Anatomy and Wood Identification	3
Packaging	2

An overview of the broad range of past and present research at FPL is found in the Laboratory's 75th Anniversary publication, "Age of Wood: Progress through Wood Research," available from Publications Distribution at the Laboratory.

Past Naval Stores Research at FPL

Research related to naval stores began in the Forest Service at the turn of the century, several years before establishment of the Forest Products Laboratory.[+] This early work was done as a cooperative effort with the Bureau of Chemistry's dendro-chemistry laboratory. At the same time, Charles Herty began a study on gum oleoresin methodology which led to the development of the cup and gutter system. Naval stores research at the Forest Products Laboratory in Madison actually began before construction of the original laboratory facility was completed in 1910. C. F. Hawley used the University of Wisconsin's heating plant for conducting research to improve the odor characteristics of wood turpentine. Research by Hawley and his colleagues on wood distillation products and on the basic chemistry of pine extractives continued over the next two decades. But by the end of that period, wood distillation was being de-emphasized. In the early 1920's, Dr. Eloise Gerry, a botanist by mining, began a thorough study on tapping methods. This work culminated in the 1935 publication of "A Naval Stores Handbook Dealing with the Production of Pine Gum or Oleoresin." During the following 25 years, naval stores research was at a low ebb with only a few studies being done in this area.

Present Naval Stores Research at FPL

The present period of FPL research in naval stores began in 1961 as a cooperative program between the Laboratory and the Pulp Chemicals Association. In general, the research effort has been at a modest level by a few senior scientists but it has been a continuing effort.

This research program has had a fundamental direction that is well-embodied in the objective statement "to improve the recovery and utilization of talk oil and related materials through a better understanding of the chemistry." To achieve this "better understanding of the chemistry," we emphasize basic research. Although tall oil and pulping byproducts are explicit in the objective statement, the relation to other sources of naval stores is equally implicit.

Based on our research experiences and on research needs, we have categorized the research efforts into three areas to indicate the primary thrust of the research. They are: Analytical development, Chemistry of recovery, and Chemistry of components. None of the areas is exclusive; most any study will have elements of all three.

Analytical Development—Our studies of analytical methodology have taken several directions. One of the major directions is in the gas chromatographic determination of the resin acid composition of rosins, oleoresins and extractives. Over the years, the analysis was accomplished with packed columns (still the current ATSM method) but most recently is done with glass or fused silica capillary columns. Gas chromatography is one of our most powerful tools in the overall spectrum of naval stores research.

[+]C. A. Nelson, "History of the U.S. Forest Products Laboratory (1910-1963)." Forest Products Laboratory, Madison, WI. (1971).

Whereas gas chromatography is most useful in detection and tentative identification of components, modem spectrochemical methods, such as nuclear magnetic resonance and mass spectroscopy, are critical in definitive characterizations of components. In the early years of my research, I purified a large number of resin acids in order to develop a reference file of spectra. However, I realized that for many of the resin acids, our 25 mg represented the world's supply of pure material. This led to sharing our spectral data in the form of a published compilation, "Diterpene Resin Acids-A compilation of infrared mass, nuclear magnetic resonance, ultraviolet spectra and gas chromatographic retention data." The compilation is extensively used in industrial, government, and academic laboratories.

In related work, we have developed a variety of analytical and separation methods such as:

DEAE-Sephadex for quantitative separation of acids and neutrals

Gel-permeation chromatography for separation of fatty from resin acids

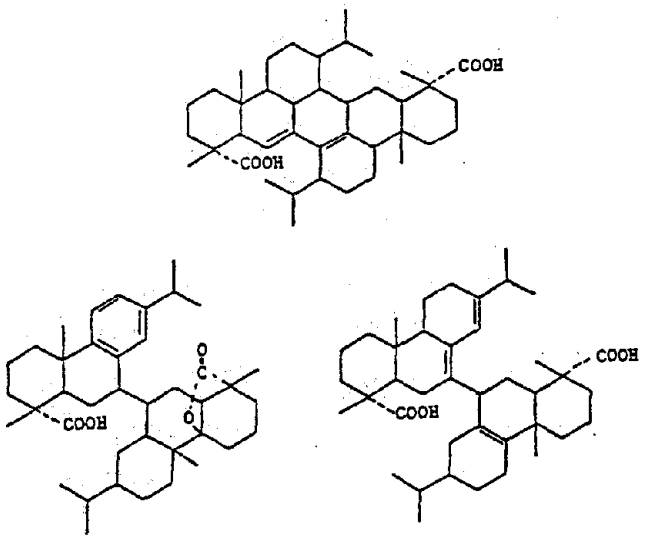
Argentative (silver complex) chromatography for the isolation of individual components

Currently, we are attempting to develop a rapid method for tall oil content in black liquor to replace the reliable, but time consuming, Buckeye method. In the future, we envision the development of naval stores analytical methods based on supercritical and countercurrent chromatography.

Chemistry of Recovery—The discovery of induced lightwood formation in the mid-1970s led to our most extensive single effort in naval stores research. The effort was 4-5 years in duration involving as many as five senior FPL scientists from several disciplines. Most of this work, as you would expect, was in cooperation with the Southeast Forest Experiment Station at Olustee, Florida. This work included the chemistry of lightwood extractives, the extent of lightwood production in a variety of conifers, the pulping of lightwood, and the physiology of lightwood formation.

Another area of extensive FPL involvement has been on the effect of storage of pulpwood chips on byproduct recovery. Of the preservative treatments that were investigated, the chemical N-methyldithiocarbamate (well known under the trade name of Vapam) was the most promising. Although the current economics of chip treatment are marginal, the research work led to the formulation by Dr. Edward Springer of chip-storage strategies for better naval stores recovery and better pulp yield. A publication on standby storage by Dr. Springer is a landmark in this area.

FIGURE 1. Three known types of resin acid dimers.



In other research on tall oil recovery, we demonstrated by use of radiochemical (carbon-14) labelling and by rigorous analytical work that the fatty acids and resin acids comprising tall can be completely recovered from pulping. But one of the major problems hindering the recovery is the absorption of the fatty acid/resin acid soaps on the pulp.

In my earlier synopsis of the history of naval stores research at FPL, I noted that the Laboratory was extensively involved in gum naval stores research. Although much of our current Chemistry of Recovery research is pulping byproduct oriented, we have been specifically involved in gum research. Most recently, we collaborated on a study with our Olustee Forest Service compatriots on the efficacy of ethylene/sulfuric acid stimulation of oleoresin flow and composition. In the course of this work, we isolated several resin acids new to those previously known to occur in slash and longleaf pines.

Chemistry of Components—I noted at the onset of this discussion of current FPL research that the three general categories are overlapping. The initial direction of an inves-

tigation of pine foliage was as a new source of naval stores chemicals and. as such. fits into the category of Chemistry of Recovery. However, the major thrust soon became the isolation and identification of a host of new diterpene resin acids. that is, an investigation of the chemistry of components. Although resin acids of pine foliage have a potential as a source of fine chemicals. the most immediate application is in insect feedant studies and in chemotaxonomy. Any further effort now in this area is of low priority. However, we have defined the opportunities in resin acid-foliage research and have devised some of the necessary analytical methodology to conduct the research.

Rosin dimers are commercially important derivatives of rosin; but until recently, little was known about the chemical structures involved. Our study of the dimerization reaction shows that several general types of dimer components are involved (Figure 1). Their chemical structures suggests that a variety of products having different characteristics can be prepared. In some related work involving the preparation of rosin polyesters as models for dimer analytical methods, we discovered a new reaction for preparing rosin ester. Of particular note is that certain esters, not possible from other methods, can be prepared.

In another study nearing completion, we investigated the composition of U.S. distilled tall oils. In the course of this work, we identified a previously unknown resin acid, the pimaric acid double bond analog of isopimaric acid, i.e., 7,15-pimaradien-l8-oic acid.

This brings me to the Texas Snow Job — a most unusual story of naval stores utilization. The Texas Snow Job, a development of the Texas Forest Service. is a method for fighting brush fires and fires in small wooded areas that uses dilute solutions of tall oil soap skimmings to produce a stable, fire-smothering foam. After the fire, the coating of foam on brush and trees has the appearance of a recent snowfall, hence the "Snow Job" name. Our contribution was in providing background information on the chemistry of soaps, chemical analysis, and in providing advice during later testing by the U.S.D.A. Forest Service.

Summary and Final Comments

In this limited time, I have provided a brief review of the naval stores program at the Forest Products Laboratory. An indication of the range of this research is reflected in a selection of publications listed at the end of this paper. (A complete list of FPL naval stores-related publications can be obtained from the author.)

The naval stores research program at the Forest Products Laboratory has a long and invaluable association with the Pulp Chemicals Association. The recent study on American distilled tall oils, for example, was a result of a PCA fellowship for a gifted young chemist. As a direct result of the FPL-PCA cooperation over the years, further cooperation has taken place with PCA member companies and their scientists, resulting in a number of publications. Other cooperative research involves other Forest Service and government laboratories, universities and colleges, and with visiting scientists and Post-doctoral fellows from the United States and overseas.

One facet of the PCA-FPL cooperation is an annual review of the research program at FPL. A recurring item of discussion is how can we maintain and improve our FPL naval stores program (particularly in these times of tightening budgets) and how can we at FPL effectively share the knowledge and expertise that we have developed over the years, beyond that achieved in our publications. Three feasible options are:

1. Visiting scientists at FPL from industry (sabbaticals)
2. Support of students at FPL; this could include summer opportunities, work-study programs, graduate and undergraduate research (thesis), and special scholarship/work-study programs at minority colleges and universities.
3. Special situations of supported cooperative research. This could include continuing research from 1 (above), three-way FPL-academic-company programs, or post-doctoral fellowships.

Some of these options have been put into practice. Working with me have been two industry scientists from Japan (for 1 year each); a post-doctoral scholar from France; short-term visiting scientists from Portugal, the Peoples Republic of China, and Mexico; and a number of graduate and undergraduate students. We plan to continue this program. I will be glad to discuss further such options for cooperative naval stores research. You can write to me at the Forest Products Laboratory, One Gifford Pinchot Drive, Madison, WI 53705-2398; or telephone (608) 264-5857. o

SOME PUBLICATIONS OF THE FOREST PRODUCTS LABORATORY

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