FINAL REPORT

PROJECT NO. 220

STUDY OF THE COMPOSITION
OF
OLEORESINS FROM PINE TREES

By

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I. SUMMARY

The Engineering Experiment Station is contemplating a long-term investigation of the nature of oleoresins from pine trees. A review of the published information on the chemical composition of oleoresins from southern pines has been conducted as an introductory procedure in establishing a basic research program on gum naval stores. For convenience, summaries of the results of this study have been presented under the headings Resin Acids, Turpentine Fraction, and Other Neutral Compounds.

Separation of the complex mixture of hydrocarbons, acids, alcohols, resenes and various other materials that make up the oleoresin has been only partially effected. Although certain major constituents are well known and characterized, many of the compounds present have not even been identified. In addition, no satisfactory methods of analysis are available for most of the constituents.

Methods suitable for isolating the individual resin acids are known, but these procedures are not sufficiently quantitative to be used as methods of analysis. Reliable procedures have been established for the quantitative determination of only one of the resin acids. Careful fractional distillation to separate the constituents of the turpentine fraction for identifying individual components has been only partially successful. Very little research has been conducted towards determining the composition of the resene portion, and only a few of its constituents are known.

Much of the research which has been done with constituents of oleoresin has been carried out on materials which have previously been subjected to rather high temperatures. This may have contributed to misleading

results since it is known that many of the primary constituents are un-
stable to heat. This fact should be considered in the development of
methods of analysis or of methods for separating the mixture into indivi-
dual compounds.

It is interesting that living pine wood contains sterols as major con-
stituents as well as relatively large amounts of fatty acids, whereas
oleoresins do not contain any sterols and only minor amounts of fatty
acids. This radical difference in the extractives of living pine wood and
the exudate of pine trees suggests that various additional compounds might
be isolated from freshly exuded gum.

A proposed method of analysis of rosin, or oleoresins, for the resin
acid components has been outlined, and some suggestions for future work
and methods which might be employed have been made.

A laboratory is being established which should prove adequate for
general organic research as well as for anticipated naval stores research.

II. INTRODUCTION

A portion of the funds made available for the fiscal year 1952-1953 for research to benefit the State of Georgia was alloted for reviewing the published knowledge about the composition of oleoresins from pine trees.

It is contemplated that the Engineering Experiment Station of the Georgia Institute of Technology will participate in a long-term investigation of the nature of oleoresins from pine trees. The program will include the identification of the various chemical constituents of the gums, the determination of methods of quantitative analysis and separation of these components, and an investigation of the changes which occur in the oleoresin constituents from the time they are produced in the tree throughout the usual processing procedures to the final products.

It is hoped that the resulting increased fundamental knowledge will be beneficial in developing new and better applications for pine gum and consequently stimulate a greater demand for this product of the gum naval stores industry of Georgia.

A study of the published knowledge about the chemical composition of pine oleoresin was undertaken as an introductory procedure toward establishing a basic research program on gum naval stores. This study was facilitated by the literature references previously compiled under Project 199. However, it was found that for some specific phases an additional literature survey was required.* Since the major species of pine utilized in

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*It is believed that additional references which prove useful for any phase of future naval stores research should be abstracted and incorporated with the card file that has been compiled under Project 199. In addition, a chemical index to this file would be of valuable assistance to future investigations of this type.

Georgia for the production of naval stores are _Pinus palustris_ and _Pinus caribaea_,* this review was limited to material pertaining to them or to methods of analysis which could reasonably be assumed to apply to the constituents derived from them. The results of this study were summarized and some future research was suggested.

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* _Pinus palustris_ Miller is known as longleaf pine, southern yellow pine, Georgia pine, hard pine, hill pine, heart pine, and longstraw pine. _Pinus caribaea_ Morelet was formerly designated as _Pinus cubensis_ Grisebach, and as _Pinus heterophylla_ (Elliott) Sudworth and as _Pinus elliottii_ Englemann. It is also known as slash pine, yellow slash, swamp pine, hill slash, and Cuban pine.

III. DISCUSSION OF THE COMPOSITION OF OLEORESINS

Pine oleoresins are complex mixtures of terpene hydrocarbons, alcohols, resin acids and resenes (nonvolatile neutral compounds) with various other materials. The oleoresins as collected at the present time consist of about four parts rosin and one part turpentine, or steam-volatile matter. A considerable amount of the volatile constituents is lost by evaporation from the tree face and collecting cups. The major constituents of the turpentine portion are well known and characterized, and several of the minor components have been identified.

The nonvolatile portion, exclusive of the acids, however, has not been so well defined. It consists mainly (approximately 90 per cent) of a mixture of resin acids with about 10 per cent resenes. The latter are a complicated mixture of aliphatic and polycyclic compounds and constitute the least known portion of oleoresins.

A. The Resin Acids*

Recent investigations concerning the nature of the resin acids present in resins and oleoresins make it apparent that the prior extensive literature pertaining to resin acids reported only a limited number of valid results. The usual techniques of isolating acid components which were employed by many earlier investigators are not satisfactory with resin acids because these acids are especially labile compounds. In addition, fractional crystallization of the acids invariably results in "isomorphous-mixed" crystals, which has led to reports of numerous "pure isomers" later shown to be mixtures. (11, 18)

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*Included under this heading are those acids of the abietic type (those acids which yield retene, or 1-methyl-7-isopropylphenanthrene, upon complete dehydrogenation and have an isopropyl or isopropylidine group at C-7) and the pimaric type (those acids which yield pimanthrene, or 1,7-dimethylphenanthrene, upon complete dehydrogenation and have the gem configuration of methyl and vinyl groups at C-7).

Applications of suitable procedures (a combination of Diels-Alder reactions and the amine-salt method of separating the acid mixtures, and an analysis based on optical rotatory and ultraviolet absorption character-istics) have resulted in an apparently complete determination of the resin acid constituents of oleoresin from Pinus palustris (11). The methods used, although valuable for preparing pure isomers, are not sufficiently exact to be considered satisfactory for quantitative analyses. It is of interest that at the present time the only reliable quantitative methods of analysis of resin acids are for the determination of levopimaric acid. These methods are based on a modification of the Diels-Alder reaction. (19)

Table I lists those resin acids which have been characterized and demonstrated to be present in oleoresin "collected from the long leaf pine, Pinus palustris, and stored at 0°-3° in the dark, and out of contact with air." (11) There remains some question about the presence of abietic acid and dehydroabietic acid as primary acids of oleoresin (32). The inclusion here of abietic acid is based solely upon an interpretation of the ultraviolet absorption characteristics of the mixed resin acids. De-hydroabietic acid is included on the assumption that its formation is coincident with the formation of dihydroabietic acid. (11)

The resin acid constituents of the oleoresin from the other major species of southern pine, Pinus caribaea, could probably be established by a parallel investigation.

Another method (colorimetric) of analysis that may be of value for certain resin acids has been reported by Tsutsui (36). The method is based upon the experimental disclosures that dextropimaric acid does not give a positive Liebermann-Storch reaction, whereas abietic and levopimaric

TABLE I

RESIN ACIDS OF GUM OLEORESIN[a]

Acid[b]	Approximate Per Cent of Total Resin Acids	Characteristics[c]	
Levopimaric (l-Sapietic)	30-35	Melting Point	143°-148°
		$(\alpha)_D^{24}$	-276°
		Maximum Absorption	272 mμ
		Specific Absorption Coefficient, α	19.2
		Melting Point of Methylester	63°-64°
		$(\alpha)_D^{24}$ of Butanol- amine Salt	-218°
		Isomerized by Heat or Mineral Acids	
Neoabietic	15-20	Melting Point	167°-169°
		$(\alpha)_D^{24}$	+159°
		Maximum Absorption	250 mμ
		Specific Absorption Coefficient, α	80.0
		Melting Point of Methylester	61.5°-62°
		$(\alpha)_D^{24}$ of Butanol- amine Salt	+162°
		Isomerized by Heat or Mineral Acids	
Abietic	15-20	Melting Point	172°-175°
		$(\alpha)_D^{24}$	-106°
		Maximum Absorption	241 mμ
		Specific Absorption Coefficient, α	77.0
		$(\alpha)_D^{24}$ of Diamyl- amine Salt	-60°
		Isomerized by Heat or Mineral Acids	

(Continued)

TABLE I (Continued)

RESIN ACIDS OF GUM OLEORESIN[a]

Acid[b]	Approximate Per Cent of Total Resin Acids	Characteristics[c]	
Isodextropimaric	8	Melting Point	162°-164°
		$(\alpha)_D^{24}$	0°[d]
		Melting Point of Methylester	61.5°-62°
		$(\alpha)_D^{24}$ of Butanola- mine Salt	0°
Dextropimaric	8	Melting Point	217°-219°
		$(\alpha)_D^{24}$	+79°
		Melting Point of Methylester	68°-69°
Dehydroabietic	4	Melting Point	172°-173.5°
		$(\alpha)_D^{20}$	+62°[e]
		Melting Point of Methylester	62°-63°
		$(\alpha)_D^{20}$ of Methyl- ester	+60°[f]
Dihydroabietic[g]	4		

[a] Gum obtained from Pinus palustris (11).

[b] The names given here are believed to be those most generally accepted at the present time. For the structures of these acids and discussions of the proof of structure see references 5, 7, 14, 16, 30, 32, and 39.

[c] Unless otherwise noted, all melting points in this report are in degrees centigrade and all rotations are of 1 per cent solutions in absolute ethanol. The specific absorption coefficient, a, is defined as: $a = $ log I_o/I_cl where $I_o = $ intensity of radiation transmitted by the solvent, $I = $ intensity of radiation transmitted by the solution, $C = $ concentration of solute in grams per liter, and $l = $ length in centimeters of solution through which the radiation passes.

[d] The same value was obtained in absolute ethanol, benzene and chloroform.

[e] This value was obtained with a 1.94 per cent solution in absolute ethanol.

[f] This value was obtained with a 2 per cent solution in absolute ethanol.

[g] Various constants have been reported for the dihydroabietic acids, and the structures of these acids have not been clearly elucidated. (See reference 39.)

acids do, and that levopimaric acid combines with maleic anhydride in
toluene at room temperature to give an adduct that does not give a positive
Liebermann-Storch reaction.

It might be well to extend the investigation of Tsutsui in conjunction
with the separation procedures of Harris and Sanderson (11, 13, 15) since
apparently the results of the latter are more complete. Carried to com-
pletion, there possibly could result a specific colorimetric method of
analysis--convenient and suitable for establishing a grading scale for
resin based upon the chemical composition.

In all probability it could be shown that the color reaction is not
actually as specific as indicated. This possibility is realized when the
reported analyses of proabietic acid (Kraft's) by the two methods are com-
pared (18, 37). It might be argued that the discrepancies have arisen be-
cause the proabietic acids were from remote sources of raw material, although
they were both prepared by Kraft's method (25); however, an additional
explanation is also apparent. Harris and Sanderson (11, 13, 15) reported
two acids as constituents of Kraft's proabietic acid which were not con-
sidered in the investigations of Tsutsui (37). One of these, isodextropimaric
acid, would be expected to behave similarly to dextropimaric.* The other,
neoabietic acid, would be expected to behave similarly to abietic or levopi-
maric acids.

It would seem that, based upon the relatively large amount of material
available concerning reactions of various resin acids, a satisfactory method
of analysis to determine quantitatively the amounts of the resin acid con-
stituents present in oleoresin or rosin could be established. Such a method

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With reference to the similarity of isodextropimaric and dextropimaric
acids, it is believed that isodextropimaric acid is actually a racemate
of two optically active acids. One of these is dextropimaric acid, the
other its still unknown optical antipod. (2) It would be interesting,
from an academic viewpoint, to attempt the resolution of isodextropimaric
acid.

which utilizes, to a large extent, known reactions is proposed in outline form and presented in the appendix. Of course, determining the validity of this proposed analysis would require laboratory experimentation.

B. The Turpentine Fraction*

This portion of oleoresins consists of approximately 95 per cent of pinenes and 5 per cent of minor constituents. The two major compounds, α- and β-pinene, are present in oleoresin from Pinus palustris and Pinus caribaea in approximately the same proportions, although reports indicate that Pinus caribaea gum contains slightly larger quantities of β-pinene. The percentage of α-pinene present in American pine gum ranges from about 58 to 68 per cent, and the percentage of β-pinene ranges from about 28 to 37 per cent, depending upon the source (6, 27). The chemistry of these two compounds is discussed thoroughly in Volume II of The Terpenes (33).

Very little was known about the composition of the turpentine fraction exclusive of the pinenes until recently when a systematic study was undertaken by the U.S.D.A. (3). By examining the first 10 per cent of the material that distilled in commercial gum turpentine production, it was determined that the maximum amount of matter boiling below the distillation temperature of α-pinene was 0.07 per cent of the turpentine fraction. No further examination was made of this forerun because of the small amount of material obtained. It is possible that oleoresins, as exuded from the tree, contain larger amounts of volatile material but that it is largely lost through evaporation. Material boiling as low as 56° C has been reported (3).

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*This designation includes those compounds of pine gum which are volatile with steam and are commonly distilled from the gum to produce commercial turpentine.

The last 10 per cent of the material that distilled in commercial gum turpentine production was examined in more detail. Careful redistillations of this material showed that about 7.7 per cent of commercial turpentine boils above the distillation temperature of β-pinene. A study of this 7.7 per cent of the turpentine fraction indicated the presence of numerous materials. It consisted of about one-fifth terpene alcohols, two-fifths monocyclic hydrocarbons, and two-fifths of a mixture composed mainly of esters and ethers.

The constituents which this study (3) and other less extensive investigations (6, 20) have disclosed, or indicated, as being present in the oleoresin of Pinus palustris are:

1. Compounds definitely identified:

    a. dipentene--boiling point: 71.7° at 20 mm. Identified through the tetrabromide derivative which melts at 124°-125°.

    b. terpinoline--boiling point: 65.5°-67° at 10 mm. Identified through the tetrabromide derivative which melts at 118°-119°.

    c. inactive bornylacetate--boiling point: about 96° at 10 mm. Identified by its hydrolysis to borneol which melts at 207°-208° and the formation of acetyl p-toluidide which melts at 148°-149°.

    d. methylchavicol--boiling point: 91.0°-91.2° at 10 mm. Identified through its oxidation to anisic acid which melts at 185°-186° and to homoanisic acid which melts at 86°-87°.

2. Compounds indicated to be present:

    a. p-menthene.

    b. a mixture of terpene alcohols, some of which are phenolic.

    c. d-limonene.

    d. alkyl ethers.

    e. esters other than bornylacetate.

    f. pinocarveol or pinocarveol hydrate--physical data on the solid materials isolated and on derivatives prepared from these materials compare fairly well with constants reported for pinocarveol and pinocarveol hydrate.

It is noteworthy that frenchyl alcohol, one of the predominate alcohols of steam-distilled wood turpentine, was not detected in gum turpentine.

A recent investigation on the aqueous phase of turpentine distillation, "low wines," has shown the presence of formic, acetic, propionic and butyric acids as well as small amounts of higher aliphatic acids-- presumably caproic, caprylic and heptanoic acids. (28) This work, although valuable in showing the presence of the various acids, is not too useful in estimating the aliphatic acid content of oleoresin itself; however, some of the techniques which were employed would probably serve well in the investigation of the composition of oleoresin.

Additional investigations of the turpentine fraction of oleoresins might well be directed to determine the composition of the more volatile portion. Such a study would require the development of methods of obtaining large quantities of gum in a manner designed to eliminate losses due to evaporation.

In addition, a more complete examination of the higher-boiling portions seems warranted. Methods of separating the constituents other than, or supplementary to, fractional distillation might be employed. It should be noted that the materials which have been examined were all previously subjected to rather high temperatures. Recent work by Kirchner and Miller (24) indicates that chromatographic adsorption techniques could be advantageously applied to these materials.

C. Other Neutral Compounds

The resenes* present in pine oleoresins consist of an intimate mixture of aliphatic and polycyclic compounds and constitute the least-known

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* Used herein to designate the neutral portion of oleoresin exclusive of the turpentine fraction.

portion of the gums. The presence of esters, dicyclic terpenes (sequi-terpenes), dicyclic alcohols, tricyclic terpenes (diterpenes), stilbenes, aldehydes (ketones?) hydrocarbons and oxidation products has been in-dicated (1, 4, 17, 19, 26, 35) although on the whole these neutral bodies have been only partially and vaguely characterized. Table II represents the data available on individual constituents that have been isolated from the resene portion of oleoresin from Pinus palustris.

It has been noted that the presence of resenes in rosin has a de-cided influence upon the reactivity of resin acids. This has been especially apparent in esterfication reactions; very small amounts of resin acid esters were obtained from rosin under conditions that resulted in good yields of esters from relatively pure acids (23). Furthermore, resenes have been shown to have detrimental effects when present in soaps

(22). It is apparent that rosin prepared in a way designed to decrease the amount of, or eliminate, the resene components would be valuable for use in the preparation of esters and soaps.

It is interesting that although sterols are major constituents of the living pine wood, they are not found in the resinified heart wood nor in oleoresins. In addition, relatively large amounts of fatty acid are present in the living wood. Since the exudate of the pine tree thus differs radically from the extractives of the living wood, and since oleoresins form readily when the tree is wounded, it has been suggested that it should be possible to isolate enzymes, precursors, intermediates, activators, or by-products from freshly exuded gums--presumably from the resene portion (19). In this connection it appears that isodextropimarinal (item 1, Table II) is probably a representative intermediate or precursor.

TABLE II

RESENE COMPONENTS

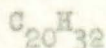|	
1. Isodextropimarinal $C_{20}H_{30}O$	This aldehyde, structurally related to isodextropimaric acid, was isolated in 4.5% yield from the neutral portion of wood or gum rosin from Pinus caribaea and Pinus palustris by Harris (17). The structure of this compound has been clearly established and it is highly probable that the "tricyclic diterpene-ketone" isolated from Scotts fir (Pinus silvestris) by Sorensen and Bruun (34) is identical to isodextropimarinal. Melting point: 50°-52° Melting point of semicarbazone: 223°-225° Melting point of 2,4-dinitrophenylhydrazone: 192°-194°.
2. An Optically Inactive Hydrocarbon $C_{27}H_{56}$	This compound was separated by Balas (1) in 0.7% yield from oleoresin (Pinus palustris) and is probably n-heptacosane. Melting point: 60° Boiling point at 12 mm.: 270° Boiling point at 0.4 mm.: 197.5° Density at 70° (referred to water at 4°): 0.7729.
3. A Tricyclic Terpene $C_{20}H_{32}$	This compound was isolated by Balas (1) from the oleoresin of Pinus palustris but was not clearly defined. Boiling point at 12 mm.: 192°-195° Refractive Index at 18°, D line: 1.5106 Rotation of a 6% solution in chloroform: +8.4°.
4. A Diterpene Alcohol	This compound from the oleoresin of Pinus palustris (1) was not identified but was shown to have the cadalene skeleton.

(Continued)

TABLE II (Continued)

RESENE COMPONENTS

5. 3,5-dimethoxystilbene	This compound has been isolated from wood rosin but not from gum rosin or oleoresins. However, it was suggested that the 3,5-dimethoxystilbene content could be calculated from the methoxyl content; this calculation would imply that the unsaponifiable portion of gum rosin consists of 0.54% of this compound (4). Unless the absence of other methoxyl compound is demonstrated, the results of this calculation can be considered only a crude estimate.
6. A "Resene"	Described as a fragile mass, this material was separated from the oleoresin of Pinus palustris by Balas (1). In all probability it represents a mixture although it reportedly melted at 117°. Rotation of a 2% solution in chloroform: +16.1°. Molecular weight: 798-830.

Even though the resene components amount to only a small portion of the oleoresins, the volume of oleoresins processed could provide rather large amounts of these compounds. The lack of knowledge concerning the nature of the resene constituents makes it impossible to evaluate the worth of this fraction of oleoresins; however, it would seem that additional research might prove that resenes contain valuable materials, e.g., the stilbenes (item 5, Table II) some of which have physiological activities similar to estrogenes'.

It would be well to investigate the possibility of utilizing chromatographic adsorption techniques as a means of effecting at least partial separation of the complex mixture that makes up the resene portion of gum.

IV. LABORATORY FOR GENERAL ORGANIC RESEARCH

In anticipation of future laboratory work in connection with the naval stores research program, laboratory space was alloted for setting up the required facilities for general organic chemistry research.

The laboratory furniture and apparatus necessary to finish equipping rooms 105 and 106 were ordered, and most of the materials have been received. Room 105 will serve as office space for two investigators and as an instrument room while room 106 will be used as the general laboratory. The sketch on the following page is the planned layout of the two rooms. The position of the proposed doorway between the two rooms, indicated in the drawing, is only approximately correct.

The instrument room will contain two desks and chairs, a file cabinet, a bookcase, a refrigerator, approximately 30 square feet of bench top for instrument space with sufficient drawer space and approximately 30 square feet of table space. The instruments for equipping this room will include such items as a Bausch and Lomb precision refractometer, a Rudolph precision polorimeter, a Fisher Micro-Gramatic balance, a Westphal balance, a Christian Becker Chainomatic analytical balance and a Hoeppler viscosimeter.

The general laboratory was planned around the existing bench in room 106 with a major addition consisting of a hood assembly made up of two four-foot hood sections with a removable panel separating the working space. The remaining floor area of this room has been reserved for equipment such as the large centrifuge and distillation columns.
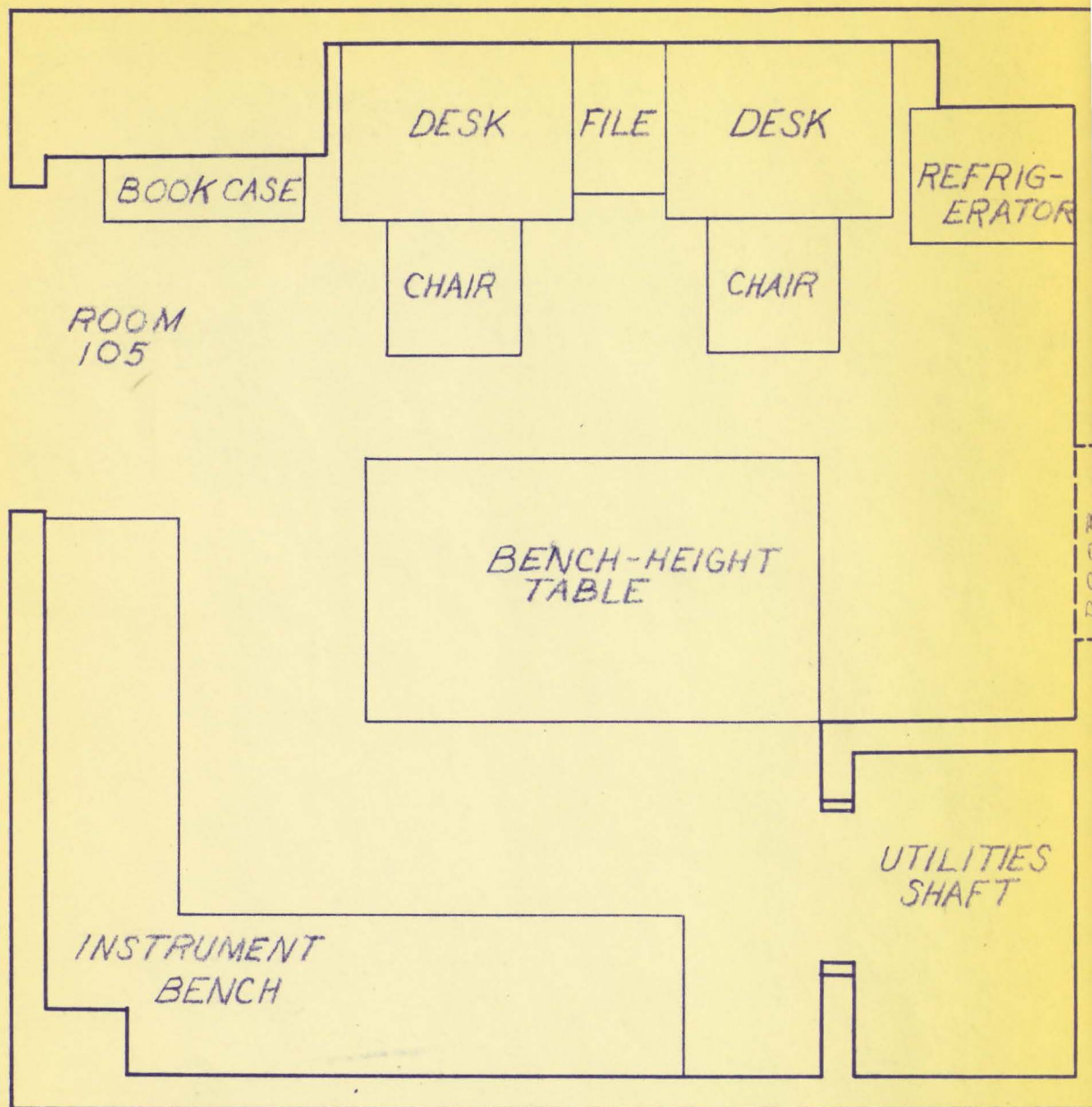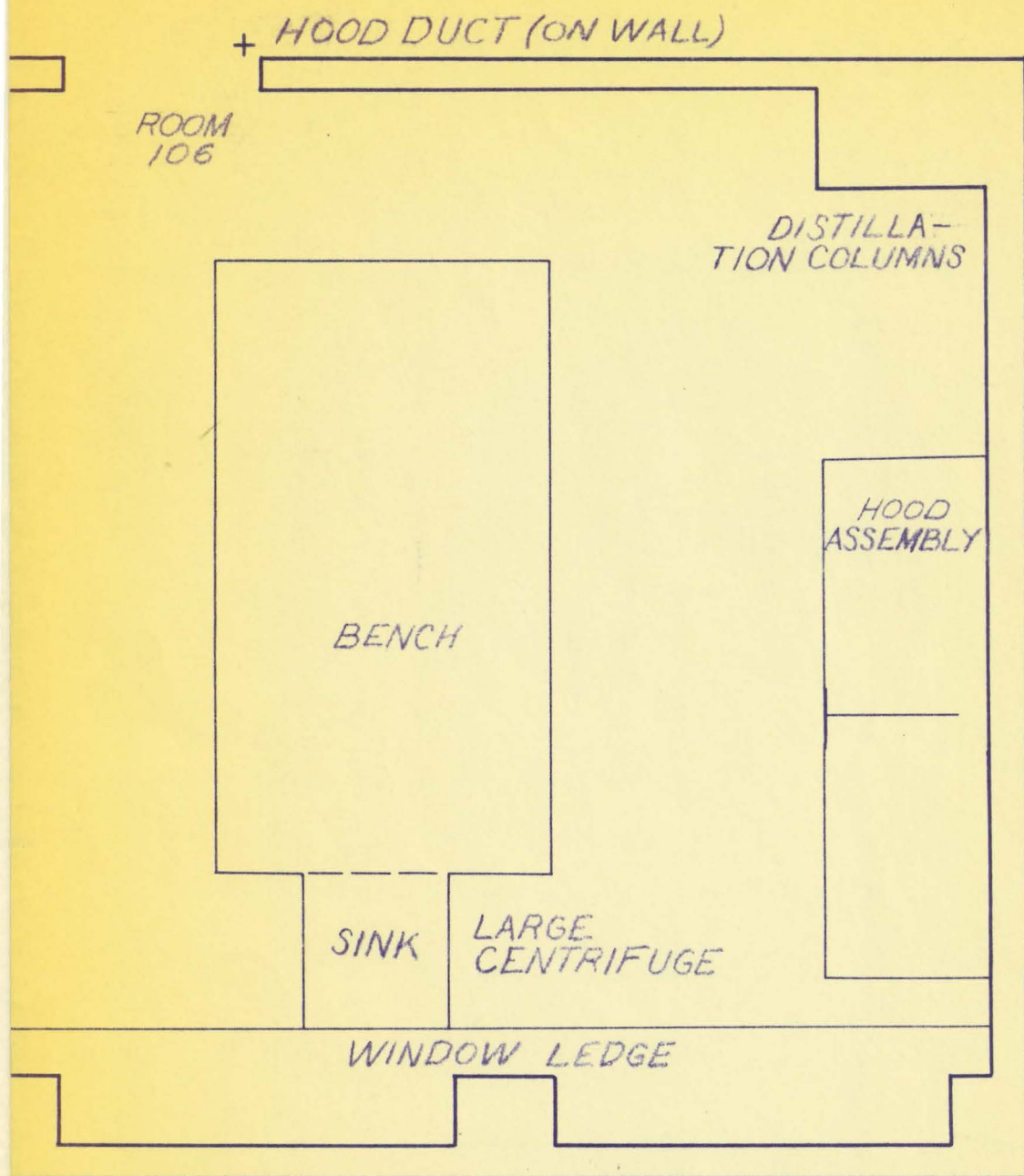
FIGURE 1. LABORA

+ HOOD DUCT (ON WALL)

ROOM
106

DISTILLA-
TION COLUMNS

HOOD
ASSEMBLY

BENCH

SINK

LARGE
CENTRIFUGE

WINDOW LEDGE

E: $\frac{3}{8}'' = 1'-0''$

TORY LAYOUT.

In addition to the usual laboratory requirements, the equipment ordered for the general laboratory included a micro carbon-hydrogen train and accessories, a micro hydrogenation apparatus, a manometric carbon combustion apparatus, a Brown boiling-point molecular-weight determination apparatus, a Todd precise-fractionation assembly, a Soxlet extractor, a liquid-liquid extraction apparatus, a Dennis melting-point determination apparatus, an International chemical centrifuge (basket type) and an International centrifuge, type I-C, with suitable heads.

It is believed that the laboratory as designed will be essentially adequate for general organic chemistry research as well as the anticipated research with naval stores.

V. CONCLUSIONS

Although considerable research has been carried out with the various portions of oleoresins, and the major constituents have been fairly well characterized, comparatively little knowledge is available concerning the numerous minor components. Much of the early investigations on the constitution of oleoresins have resulted in doubtful reports because of the nature and history of the primary compounds present.

Suitable methods are available for isolating pure individual resin acids from the nonvolatile portion of gums, but these procedures are not quantitative. Feasible processes for the quantitative determination of the resin acids (with the exception of levopimaric acid) remain to be developed.

The nonacidic parts of the nonvolatile portion of oleoresins are largely uncharacterized. In addition, the volatile components, exclusive of the pinenes, have been only partially identified.

Practically all the experimental work that has been conducted with the nonacidic portions has been carried out on material which had previously been subjected to rather high temperatures. Since it is known that many of the terpene components are unstable upon heating, this may have caused erroneous results. Methods of separating and analyzing for the components of oleoresins will have to be developed, taking into account the probable sensitivity of the constituents.

It is believed that sufficient information is available concerning the reactions of the resin acids to warrant experimentation toward developing a quantitative method of analysis of rosin, or oleoresin, for the resin acid components.

Respectfully submitted:

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Approved:

Herschel H. Cudd, Director
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APPENDIX

PROPOSED METHOD FOR THE ANALYSIS OF ROSIN*

INTRODUCTION:

At the present time rosin is graded only by comparing its color to standard references (blocks of rosin, plastic, or glass plates). This crude method is not adequate for many uses, particularly those which involve chemical modifications. An additional grading scale based upon the chemical composition would be valuable. This would require the development of a suitable method of analysis for the constituents.

It would seem that, based upon the relatively large amount of material available concerning reactions of the various resin acids, a satisfactory method of quantitative analysis of the resin acid constituents of rosin could be established.

Such a method which utilizes, to a large extent, known reactions is proposed. Determining the validity of the proposed analysis would require laboratory experimentation.

SUGGESTED PROCEDURE:

The proposed method is given schematically in Figure 2.

The method of titrating to determine total acids (A) is an accepted procedure and is described in detail for oleoresin by Fleck and Palkin (9) and for rosin by Smith (34).

Treatment of a gasoline solution of rosin acids with cyclohexylamine (B) reportedly results in nearly quantitative precipitation of the acids as salts. (12, 13.)

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* This procedure should also be applicable to the analysis of the acidic components of oleoresins with only minor changes.

Rosin   (A)
Titrate with 0.5 N
alcoholic KOH → Total acids
and therefore
total non-
acidic mate-
rials

(B)
Cyclohexylamine

Total acids as salts

(C)
Boric Acid

Regenerated total acids

(D)
Maleic anhydride
in acetone at 20°

(E)
Maleic anhydride refluxed in
toluene (with mineral acid or
ultraviolet light)

(F)
Controlled catalytic
hydrogenation.
H$_2$, Pd Charcoal,
20°   1 hr.

Levopimaric
acid

Total conjugated-two-
double-bond acids (levo-
pimaric, abietic and neo-
abietic)

Total external double bond
acids (dextropimaric,
isodextropimaric and
neoabietic)

(G)
Reaction product with maleic anhydride
refluxed in toluene (with mineral
acid or ultraviolet light)

Remaining conjugated-two-double-bond
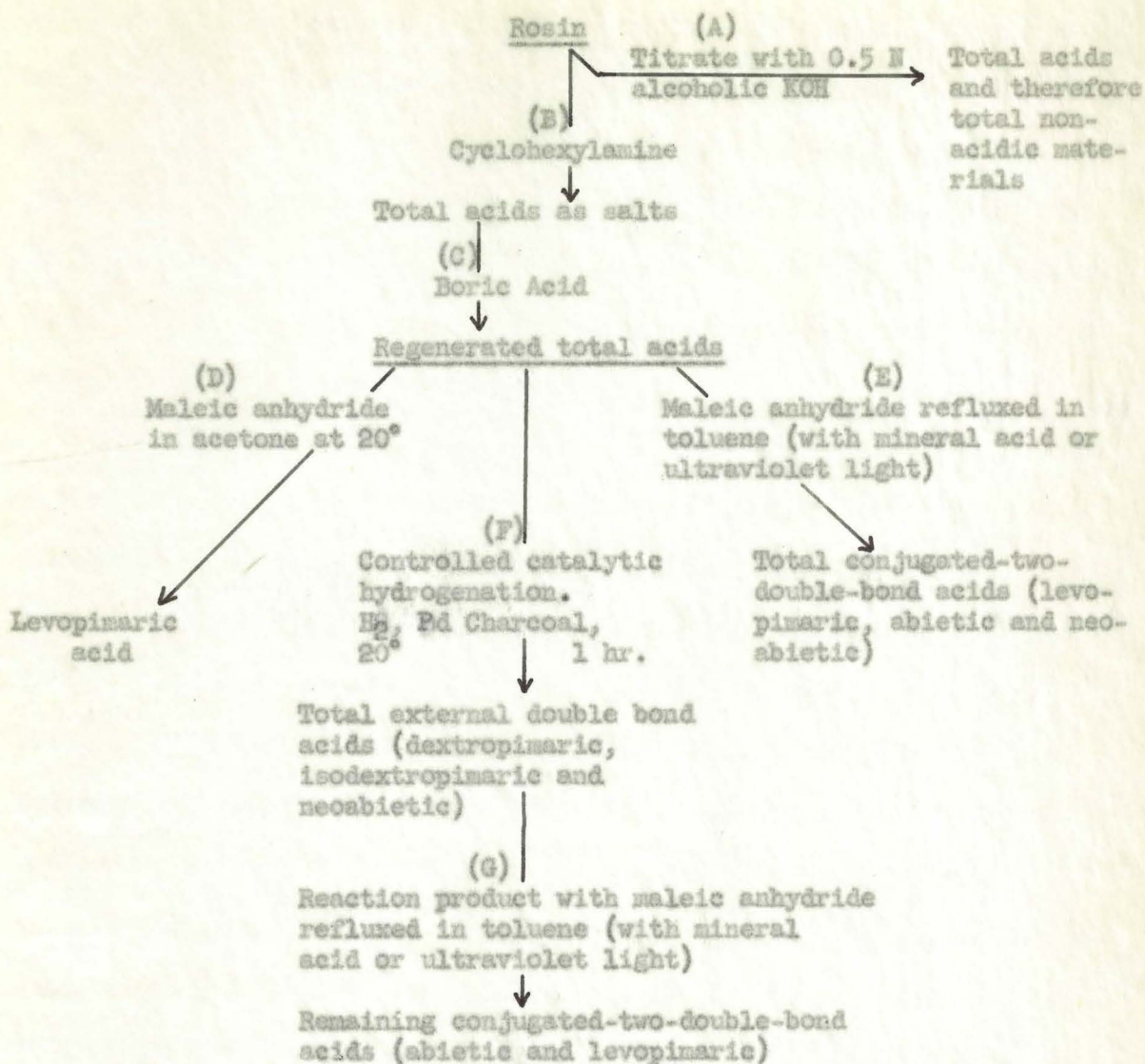acids (abietic and levopimaric)

FIGURE 2. PROPOSED Analysis of Rosin.

The acids can be conveniently regenerated unchanged from these salts by treatment with boric acid (C) under proper conditions. The regenerated acids should be dried and weighed. This determined weight should correspond to the weight of total acids as calculated from the potassium hydroxide titration. It is believed that the cyclohexylamine salt procedure will be sufficiently quantitative; however, it may be that amounts of solvent smaller than have been used will be necessary or that a different amine and/or solvent will have to be selected.

The indicated method (D) for the determination of levopimaric acid has been reported and generally accepted as being reliable. The calculations can be based upon the amount of maleic anhydride used in the reaction, the weight of adduct formed (9) or upon changes observed in optical rotatory power (11). It would be well to compare all three methods to determine the most convenient procedure. Probably the most satisfactory determination will involve the extraction of the excess maleic anhydride as maleic acid and titrating with a standard base.

It should be possible to determine the total conjugated-two-double-bond acids by a similar reaction (E) with maleic anhydride at elevated temperatures in the presence of mineral acid or intense ultraviolet irradiation (38). The mineral acid or light catalyzes the isomerization of the acid components and thereby would increase the rate at which the maleic anhydride would adduct. Calculation of the amount of these acids (levopimaric, abietic and neoabietic) present would be based upon the amount of maleic anhydride that reacted or the weight of adduct formed. (It is not apparent in this case how changes in optical rotation might be utilized.) If the determination is based upon the amount of adduct formed, assuming that experimentation would show that the adduct is sufficiently insoluble, either mineral acid or ultraviolet light could be used as a catalyst. If,

however, the excess maleic anhydride is to be determined by titration, the catalyst would have to be ultraviolet light in order to avoid the complications of having a mineral acid present. (In a nonaqueous solvent, the amount of mineral acid would not be expected to remain constant throughout the necessary refluxing.)

By selecting proper conditions, it should be possible to hydrogenate quantitatively the external double bonds in the total resin acids mixture without effecting the reduction of the ring double bonds (F). The conditions suitable for such a reduction are indicated by the work of Harris on the structural determination of isodextropimarinal (17), dextropimaric acid, and isodextropimaric acid (16). (Five grams of the acid were hydrogenated in the presence of one gram of five per cent palladium-carbon catalyst with ethanol as a solvent for approximately one hour at room temperature. With the aldehyde a one-to-one ratio of catalyst to aldehyde was used and the solvent was methylcyclohexane.) It would be necessary to check the reduction of neoabietic acid under these conditions to determine whether the reduction proceeds as desired. The structure of neoabietic acid indicates that such would be the case; however, some modification of this procedure may be necessary. From this hydrogenation, the amount of acids present which contain external double bonds could be calculated by determining the quantity of hydrogen used in the reduction.

The reaction mixture from the above reduction should contain only two acids capable of adducting with maleic anhydride (abietic and levopimaric). Using the methods previously outlined, the combined amounts of these two acids could be determined (G), i.e., reaction with excess maleic anhydride in presence of catalyst and titration of excess maleic anhydride.

By examining the values determined in this procedure it would be possible to ascertain the amounts of levopimaric, neoabietic, and abietic acids present in the rosin as well as the combined amounts of dextropimaric and isodextropimaric acids. (This combined value should be sufficient for practical purposes since isodextropimaric acid is apparently a race-mate of dextropimaric acid with its optical antipod, so these compounds would behave identically in chemical reactions not involving certain optically active compounds.) In addition, the difference between the total acid content and the total of the values of the individual acid components detected would represent the combined amounts of any dihydro and dehydro acids present. Since these acids apparently are formed by disproportionation of primary acids, the value of each would be one-half the combined value.

Should laboratory experiments prove the described procedures, or modifications of them, to be sufficiently quantitative, an essentially complete quantitative analysis of rosin could possibly become a routine practice.

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