

On Pine Tree Resenes¹

In the Biogenesis of the Resin Acids

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Abstract

The variations in composition of extractives obtained from various parts of the pine tree are emphasized. The nonsaponifiable part — the resenes — in these mixtures contain a series of compounds, which show an interesting diversification of physiologic action. Extended research should be inviting in this very little known field of pine tree resenes, considering their potential value as an untapped source for the production of vitamins and synthetic hormones.

Presentation is made of a new carbonyl compound occurring in crude tall oil soap in amounts of 10% of the total resenes content. This constituent is tentatively identified as a ketone and named: "Tall oil ketone."

In view of the more rapid progress in the adjacent fields of resin acids, sterols and terpenes, the Sander-mann hypothesis for the biogenesis of the resin acids from phytol is discussed and suggestions made for its simplification. It is believed that new applications of these concepts may aid practical research in this largely unexplored field of wood chemistry.

The transformation of pine tree sapwood into heartwood is associated with vital changes in the composition of the acidic components present in the turpentine free resinous extractives of pine wood. Equally radical changes occur in the nonsaponifiables—the resenes part—of these extractives. Wounding of the pine tree produces an exudate almost instantaneously and in abundant quantities in certain species at favorable seasons. This exudate—oleoresin—and the resin of resinified heartwood are devoid of fatty acids and sterols, although these products are in the majority nonaqueous components of the resin in the growing part of the tree. Thus, it would appear that the biogenesis of the resin acids occurs at the expense of the fatty acids and sterols in the sapwood extractives. Some years ago, it was suggested that this phenomenon might be effected by a "carcinogenic process". While proper recognition was given to the remarkable speed, by which this process is taking place, pointing to the action of enzymes, it was

assumed that this transformation might also be due to the sterols present, by reactions yet unknown; the close chemical interrelationship between resin acids, sex hormones, carcinogenic substances and certain vitamins being established by organic chemistry (15).

Recent investigations on the membrane substances of wood have revealed the existence of a large family of physiologically important phenolic compounds, which are present in almost insignificant quantities. These lignanes and pinosylvins contain the same nuclear components as lignin and have, therefore, been suggested to be the precursors of lignins and tannins or by-products produced in the biogenesis of these materials.

The amount of resenes in pine wood is equally small. This group of compounds is isolated by ether and subsequent petroleum ether extraction of the saponified portion of pine extractives. The resenes are a complicated mixture of aliphatic and polycyclic compounds and constitute the least known series of pine wood components.

The resenes obtained from different parts of the pine tree vary greatly in composition. In Table I are summarized the percentage content of fatty acids, resin acids, resenes, and sterols present in commercially available products obtained from different parts of the pine tree. References to more detailed information about variations of the resenes, fatty acid and resin acid content of pine tree extractives will be found in the cited literature (9, 33, 34). (See Table I below).

On investigating "Pine Bark Flour" of Finnish origin, Pajari (35) identified in the resenes part beta-sitosterol, dihydrositosterol, lignoceryl alcohol and arachinyl alcohol, and observed a carotene content of about 0.0032% in this material. An isomer of squalene was also identified, which on ring-closure yielded monocyclosqualene. These "Pine Bark Flour" resenes also contain saturated and unsaturated hydrocarbons of the C₂₁ and C₂₆ series in addition to minute quantities of oxygen containing solids of unknown structure. However, through chromatographic adsorption, these compounds were separated into individuals and analyzed for the empirical composition: C₁₄ H₂₄ O; C₂₀ H₄₀ O, C₂₅ H₄₀ O and C₂₅ H₄₂ O.

Sandquist and his coworkers (40, 41, 42, 6) identified beta-sitosterol, dihydro-sitosterol and lignoceryl alcohol

TABLE I

Name of Resin	Fatty Acid Content	Resin Acid Content	Resenes Content: Total	Sterols	Origin
1. Resin from Finnish "Pine Bark Flour" (35) *; **	63%	17%	20%	10%	Extractives of air-dried and ground inner bark of <i>Pinus sylvestris</i> (Scots pine)
2. Tall oil (42)	28.4-50.6%	34.5-52.2%	12.1-18.5%	3-4%	<i>Pinus sylvestris</i>
3. Tall oil (28)	42.5-55.6%	38.8-52.2%	5.1-7.4%	2.6-3.7%	<i>Pinus palustris</i> and <i>Pinus heterophylla</i>
4. Gum rosin	None	92%	8%	None	Species as in 3.
5. Wood rosin	None	90%	10%	None	Species as in 3.

* According to Tigerstedt (44), the nutrition value of Finnish "Pine Bark Flour" is 45% of that of rye flour of the same moisture content. Since time immemorial, the natives in the Northern hemisphere on both sides of the Atlantic were known to have substituted grain flour by "Pine Bark Flour." Mention of this emergency food is made by the Finnish national epic "Kalevala," in Russian chronicles of 1128 A.D., and by the British geographer MacKenzie, who about 1790 travelled in Northwestern Canada, exploring the river now bearing his name.

** Investigations are lacking to show whether or not "Pine Bark Flour" from American trees, potentially available in enormous quantities, could be employed as a diluent for grain flour in case of an emergency or used as animal feed at normal times.

in the resenes of tall oil obtained from Scots pine. Lignoceryl alcohol was anticipated, and beta-sitosterol was found to be the chief component of the tall oil resenes of Southern pine (16, 17). Acetoguacone was identified in tall oil from Scots pine by Swedish chemists (7).

Although traces of sterols have been detected, no information is as yet available about the presence or absence of vitamins in resenes of pine oleoresin, gum or wood rosin. According to Balas (3), the resenes of rosin are a mixture of di- and triterpenes, polyterpene alcohols and aliphatic hydrocarbons with more than twenty carbons to the molecule. Small quantities of methylated 3,5-dihydroxystilbens — pinosylvins — were found in the resenes of American wood rosin (10). Noteworthy is the recent discovery of Sorensen and Bruun (43) that the resenes of Scots pine contain a solid unsaturated ketone "cryptopinone," m.p. 50 to 52°; semicarbazone m.p. 223 to 224°, because it analyzed for $C_{20}H_{30}O_2$ or $C_{20}H_{32}O_2$, which bears a close relationship to the empirical composition of the resin acids $C_{20}H_{30}O_2$ of pine tree rosin.

It is of interest to note that a number of the components present in the pine tree resenes are physiologically active or attain this faculty when subjected to relatively simple chemical reactions. Of pharmacologic interest is the presence of carotene as precursor of vitamin A and the possibility that the sterols of pine tree resenes might serve as an inexpensive raw material for the making of synthetic sex hormones and vitamins (16, 35). Some of the demethylated lignanes and pinosylvins are highly active; the latter group are powerful fungicides and bactericides (12); nor-conindrin is an effective antioxidant (13). Methylated pinosylvins have been isolated in wood rosin resenes (10), but no evidence is available as yet, that pine resenes would contain derivatives of conindrin (sulphite lactone).

To this information on the constituents of pine tree resenes the following new material is added on the tall oil nonsaponifiables:

On employing substantially the same procedures as recommended by Sandquist (loc. cit), but using crude tall oil soap as raw material such as received from kraft pulp mills, it was ascertained that the solid tall oil resenes originating from southern pine have approximately the following composition: 63% beta-sitosterol, 7% dihydrositosterol and 30% lignoceryl alcohol. This establishes the fact that the components of solid tall oil resenes from southern pine and Scots pine contain the same products.

By using the Girard reagent on the liquid resenes portion, a liquid, high-boiling carbonyl compound was obtained. The yield was about 10% of the total tall oil resenes. This compound* is stable to distillation in vacuum, which fact made it easy to carry out the isolation directly from the crude liquid tall oil resenes by fractionally distilling in vacuum without a column and collecting the fraction boiling at 163 to 173° 2mm (uncorr.). The compound was then purified through the semicarbazone, which was hydrolyzed and the residual oil fractionated. The carbonyl compound gave negative tests on aldehydes with the Tollens' and Schiff's reagents. Likewise, the bromine test for unsaturation remained negative. Despite this author's experience that some terpene aldehydes and aldehydes of the resin acid group do not readily respond positively to the aldehyde

* Will be subject matter for a separate paper by Hasselstrom, Stoll, and Bourke.

tests, it is assumed, until further evidence is available that the new carbonyl compound is a saturated ketone, "tall oil ketone", and not an aldehyde, considering that the tall oil soap in the kraft pulp mill digester had been subjected to a treatment with alkali which normally would lead to transformation of aldehydes according to the Cannizzaro rearrangement (30).

The "tall oil ketone" showed the following characteristics: "tall oil ketone", b.p. 163 to 167° 2mm (uncorr.); "tall oil" ketosemicarbazone, m.p. 193° (decomp'n), melted at 198 to 201° (at strong decomp'n); "tall oil" keto 2,4-dinitrophenylhydrazone, m.p. 169.5 to 171° (uncorr.), on once crystallized material.

On refluxing "tall oil" ketone with acetic anhydride, an acetate was obtained. This acetate yielded, on saponification with alcoholic potassium hydroxide, a compound which lacked the carbonyl group. This unexpected result points to the fact that the acetic anhydride treatment of the "tall oil ketone" had caused keto-enol isomerism by forming an alcohol, which combined to form an ester of acetic acid.

The resenes content and the other components of tall oil from southern pine vary as to place of growth but insignificantly as to seasons. This was recently shown by Jennings (28). Scandinavian tall oil from Scots pine has about the same general composition as American southern pine tall oil but shows greater variations in composition as to locality of growth. Sandquist (42) was able to show, as evidenced from the maximum and minimum percentage figures on the components of *Pinus sylvestris* in Table I, that Scots pine grown about the Arctic Circle produces a tall oil of a rather high percentage in resenes and fatty acids at the expense of the resin acids. This phenomenon is attributed by Scandinavian kraft pulp mills in Lapland to the slow growth and dense lumber in countries with a short growing season and prolonged low temperatures at winter time. These findings may invite crossbreeding of pines to obtain species having extractives of high fatty acid content especially in the Scandinavian countries, where tall oil is an important source of drying oils.

Since the formation of oleoresin takes place promptly, it would seem possible to find and isolate in the resenes mixture active compounds which, besides enzymes, are precursors, intermediates, activators or byproducts or in some other way responsible for producing an exudate differing radically in composition from the extractives of the living tree.

As shown from the preceding paragraphs, our present knowledge about the pine tree resenes' composition is limited. Giving recognition to the fact that the resenes quantitatively represent an immense potential commercial source of readily available sterols and vitamins (15, 16, 35), and to the rapid progress in the adjacent fields of resin acids, polyterpenes, lignanes, pinosylvins, etc., it may be justified to review a hypothesis on the biogenesis of the resin acids as a means of facilitating future investigations dealing with the resinous extractives of pine wood.

Sandermann (39) suggested in 1938 phytol I to be the precursor of the resin acids. According to his hypothesis, the aliphatic terpene alcohol containing twenty carbons, to the molecule may, by ring closure, produce a diversified line of important naturally occurring compounds: on monocyclization, vitamin A, II; on dicyclization, sclareol III and manool IV, agathic acids V, the resin

acids of Manila and Kauri copal, etc.; on tricyclization, the resin acids VI, VII of pine tree resin.

It is of interest to recall that vitamin A, II is extremely sensitive to mineral acids (11), which change apparently involves partial cyclization to sclareol III and manool IV type of compounds. It would seem that this observation bears a relationship to the well known phenomenon used in practice, namely, that mineral acids greatly stimulate the flow of oleoresin. Vitamin A is exactly one-half of the beta-carotene molecule (31). The possibility that the carotenes may originate from phytol on dehydration, subsequent dimerization and partial cyclization does not rule out the fact that some of these reactions might be reversible in the biochemical reactions occurring in the plant and might be causing the formation of resin acids with the carotenes and vitamin A or their analogs as likely intermediate compounds, Table II.

Sandermann (loc. cit.) suggested that the biogenesis of the resin acids is due to "methyloxidation", hydration, dehydration and vinyl carbinol isomerism. By introduction of the concept of methyloxidation, which readily occurs in the animal body according to Kuhn (29), an appropriate amendment was found to Aschan's (1) earlier suggestion about the formation of the resin

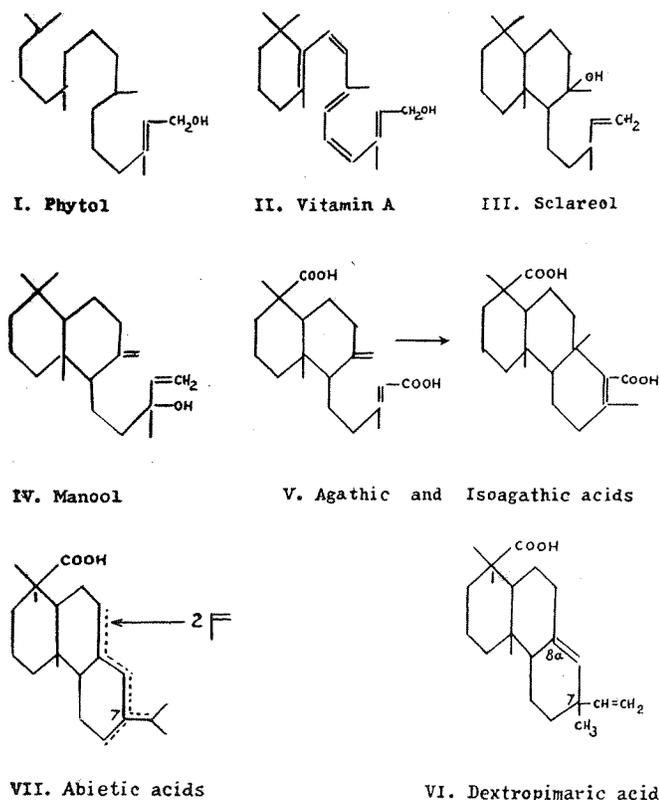
mer of phytol rather than phytol itself to be the precursor of the resin acids. It was also necessary for him to assume rather complicated reactions, for the formation of the isopropyl and vinyl side-chains in the resin acid molecules. Some of the criticisms to the Sandermann theory arose from the significance he assigned to the vinyl carbinol isomerism in the transitions involved in producing the vinyl side-chain of dextropimaric acid VI and the isopropyl group of abietic acid VII. The reason for this objection is easily understood from the fact that at that time no exocyclic unsaturated groups were known to exist in the unstable abietic acid series, although this type of unsaturation, as well as stability, were the main characteristics of dextropimaric acid. Yet, Sandermann's suggestion proved fruitful in the further investigations on the identity of the resin acids in pine tree resin.

Through the excellent work of Harris and coworkers (23, 22, 24), two other resin acids having the exocyclic unsaturation were isolated from rosin of southern pine, namely, neo-abietic acid and isodextropimaric acid. The preparation of the former was recently described in the literature (22, 23). These results constitute a valuable support to the Sandermann hypothesis. The procedure employed by the Harris group comprised an improved use of selective precipitation and fractional crystallization of various amine salts of the resin acids, a method originated by Balas (4) and applied on a smaller scale by other workers in the field (14, 18, 19, 20).

The discovery of ketones in the resenes part of the pine tree extractives is apparently of interest both from the practical and theoretical point of view. That the "tall oil ketone" or aldehyde, due to an unstable hydrogen atom, is capable of keto-enol isomerism might become of particular significance for our understanding of the biogenesis of the resin acids. While no proof is available whether or not this carbonyl compound is or could be an intermediate in the formation of the resin acids, its mere properties suggest, that the resenes of the pine tree may contain components having the prerequisites of undergoing the intramolecular rearrangements, which heretofore have been attributed to the turpentine components of the pine tree, and which cause the synthesis of fenchylalcohol and borneol found in the pine oil, or to the "1.1" substituents in the resin acid series.

The Wagner-Meerwein rearrangement has been applied by Ruzicka and coworkers on the substituents in the "1.1" position of abietic acid VIII (36, 38), on isoagathic acid V. (37) and in the podocarpic acid series by others (8).

Recent literature suggests that both the dextropimaric acids and the abietic acids are substituted in the same "1.7" positions of the partially hydrogenated phenanthrene nucleus (Harris et al.) loc. cit.: Zeiss (48). The "7" instead of the "8a" position for the vinyl side-chain of the dextropimaric acid is preferred, as agreeing better with the isoprene rule. No absolute proof is available as yet, that the "7" position is established for the vinyl group, although the results of Barker et al (5) and of Hasselstrom et al (21) strongly support such a supposition (48). These considerations should lead to a reinvestigation concerning the true position of the "8a" gem-methyl-group in isoagathic acid. However, if the vinyl group of dextropimaric acid is in the "7" gem-position, then it seemingly would be possible, due to the

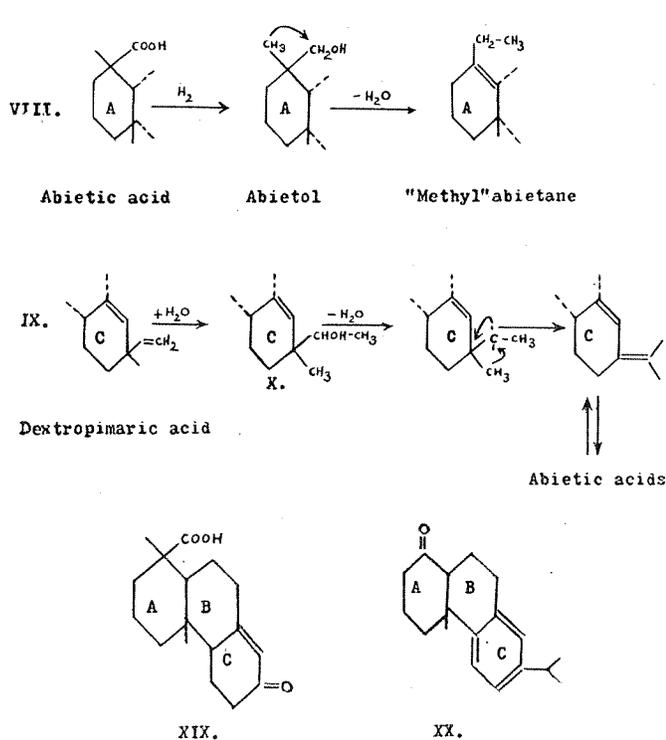


acids. Aschan (loc. cit.) suggested that the resin acids might originate from co-polymerization of isoprene and vinylacrylic acid. While of interest to practical polymer chemistry this assumption did not explain the biogenesis of compounds which do not have the carboxylic group in the gem-position, as for instance, agathic acid, etc.

Since Sandermann (loc. cit.) assumed the vinyl side-chain of dextropimaric acid VI to be in the "8a" position, and the isopropyl group of abietic acid VII in the "7" position, it was necessary for him to suggest an iso-

experience with the side-chain in the "1.1" position of undergoing the Wagner-Meerwein rearrangement, to convert the dextropimaric acids into abietic acids by applying the Berthram-Walbaum hydration reaction or the Reychler (35a) version thereof, IX. The Berthram Walbaum reaction comprises the addition of water to molecular systems capable of producing the Wagner-Meerwein pinacolone rearrangement.

Since this concept could be of practical use, the suggestion is made that the application of this reaction in the resin acid series may not only render unstable pine tree rosin and tall oil resin acids stable to oxidation, but also create starting materials for interesting synthetic resins of new types. It may be recalled that Aschan (2) in studying this reaction on the resin acids of tall oil was able to show, as expected, that the addition of water causes formation of optically inactive compounds indicating the possibility of an intramolecular rearrangement. Regardless of whether or not neo-abietic acid was originally present in this unstable tall oil resin acid mixture, it would seem entirely possible that the exocyclic isopropylene side-chain may have been formed and which reacted abnormally in a manner as previously reported occurring in the true terpene series causing an intermediary addition of sulphuric acid to form a stable furane ring on further processing (45). The importance of this type of reaction is of obvious interest to the industrial chemist, since it might offer a new approach to the use of rosin in synthetic resin manufacture.

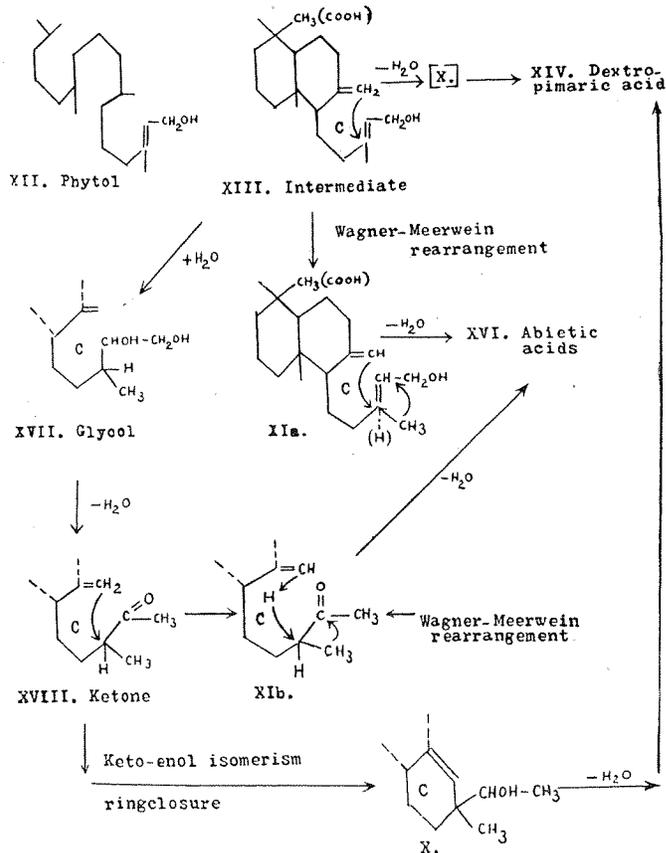


Lately, the Sandermann hypothesis about the biogenesis of the resin acids from phytol has gained additional support through the partial synthesis of dehydroabietane by Jeger and coworkers (27). These chemists were able to demonstrate that manool IV has the same steric configuration as has abietic acid. Manool is the main component in the resenes of *Dacrydium colonsoi* (25) and *Dacrydium biforme*, (26), which are yew-like

shrubs. The relationship of manool to phytol, the resin acids and agathetic acids, etc., is elucidated by formulas I to VII; it fosters the suggestion that an intermediate XIII, having 2 or 3 double bonds and a skeleton analogous to that of agathic acid V, might be the precursor of the resin acids or oleoresin. Such a compound would apparently be closely related to vitamin A, II.

Assuming that dextropimaric acids and the abietic acids are substituted in the same positions of the phenanthrene nucleus, and that the Wagner-Meerwein retro-pinacolone rearrangement may occur in the resenes mixture, the Sandermann hypothesis for the biogenesis of the resin acids might consequently be amended so as to comprise the formation of dextropimaric acids from phytol by "Methyl oxidation," ring-closure analogous to the conversion of agathic acid into isoagathic acid V, citronellal into isopulegol, by Bogert and Hasselstrom, (7a), and dehydration: XII—XIII—XIV; and abietic acid by "methyl oxidation", ring-closure, and a Wagner-Meerwein intramolecular rearrangement on dehydration at the closure of the ring "C", without the dextropimaric acid type being a necessary intermediate: XII—XIII—XIa—XVI, and accompanied by a shift of double bonds similar to that described in VIII.

According to Sandermann (loc. cit.) reactions of hydration and dehydration are involved in the biogenesis of the resin acids. Thus, the intermediate vinylcarbinol XIII, may hydrate to form glycol XVII, which on dehydration would yield a ketone XVIII. On account of



their steric configuration, ketones of this type would render themselves open to keto-enol isomerism and subsequently might produce dextropimaric acids XVII—XVIII—X—XIV on additional dehydration, and abietic

acids on Wagner-Meerwein rearrangement, XVIII—XII—XVI, or be stable products of the type XVIII.

Recent work on the side chains in the abietic acid nucleus has revealed that these may be replaced by the keto group. Harris and coworkers (23, 24) were able to produce a "nor-resin acid ketone" XIX from neoabietic acid by removing the isopropylene group through selective ozonation. Zeiss (47) obtained "nor-dehydroabietone" XX on chromium trioxide oxidation of diphenyl-t-dehydroabietenol.

In view of these results, the suggestion is made that a comprehensive study on the migration of substituent groups in the pinacoline and retropinacoline rearrangements applied to these ketones may lead to interesting partial and complete syntheses of the principal groups of the resin acids and of synthetic hormones, isomers to those now derived from sterols. The practical result of such investigations would be the introduction of the inexpensive resin acids as raw materials for new diversified series of highly priced physiologically active compounds to be employed in the pharmaceutical and insecticide fields.

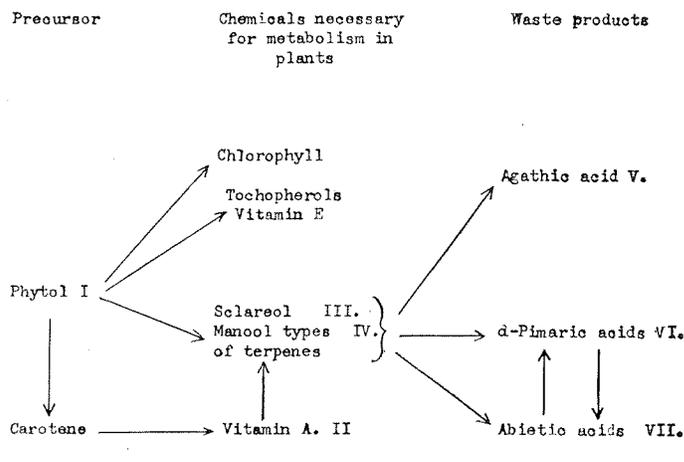
The composition of the pine tree resenes as shown in Table I indicates that, no matter in which part of the tree they originate, the resin acids are exuded on wounding of the tree or are progressively accumulated in the dead parts, namely, in the heartwood, from which they are not removed by any biological processes. Thus, it would seem likely, that the resin acids are materials which the tree, in the process of natural metabolism, tends to remove as waste products, when not needed for protection. If the Sandermann hypothesis is a valid one, namely, that phytol is the precursor of the resin acids, then the fatty acids and sterols must be assigned another task, not yet understood, in the metabolism of the tree. Furthermore, if phytol is the key compound in the biogenesis of the resin acids, other biological processes occurring in the pine tree, are apparently related to the process of resinification. The role of phytol as the possible precursor of important biochemical syntheses taking place in the plant may hence be discussed as shown in Table II. The laboratory synthesis of alphatocopherol, vitamin E, from phytol was successfully accomplished by Karrer (32). Phytol is the one-third part of chlorophyll, in which it, according to Willstaetter (46), is contained as the alcohol component.

Could it be that resinification and leafing of the tree are based on the same general principles? Certain similarities apparently do exist. The spring leafing of hardwoods is accompanied by a sudden outburst in biological activity, seemingly not much different from that of the oleoresin produced on scarification of pines. The leafing of pines is a slow process. Thus, it would appear that the pine tree is continuously diverting surplus phytol, not needed in the biogenesis of chlorophyll, carotene, etc., towards the formation of resin acids to be deposited in the heartwood or to be exuded from the tree in the oleoresin as "protective waste materials."

Acknowledgment

The author wishes to express his appreciation to the U. S. Industrial Chemicals, Inc., for releasing this new material on tall oil resenes, which is part of a comprehensive investigation. Heartfelt thanks are also due to Miss Virginia D. Bourke and Mr. Michael Stoll, Research Chemists of the above Company, for their interest and aid in the experimental work.

TABLE II



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