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THE RESINS AND THEIR CHEMICAL RELATIONS TO THE TERPENES[1]

THE closing years of the eighteenth and the beginning of the nineteenth centuries found chemists engaged in the study of chemical problems related to both plant and animal life. Organic chemistry during this early chemical epoch was exactly what its name implied, a study of those substances which are produced through life processes, either plant or animal. During this early epoch, the problems in plant chemistry were more inviting to the chemist than those in animal life, first, because the compounds appeared to be simpler substances and, second, because they crystallized more readily and were therefore more readily obtained in pure form. As a result of these characteristics, early organic chemistry was largely confined to plant life, consisting, however, of little more than the simple preparation of the substances themselves.

Scheele was the first to point out that the plant and animal world is made up of definite compounds, just as is the inorganic world. He proved the assertion by isolating a number of organic substances, among them tartaric, citric, malic and uric acids. He even went so far in his study of the organic compounds as to suggest what the modern physiological chemist calls metabolism, as a means of explaining certain physiological processes. Owing, however, to the extreme difficulty in obtaining physiological compounds in crystalline

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[1] A part of the address of the vice-president and chairman of Section C, American Association for the Advancement of Science, Washington, December, 1912.

form, Scheele devoted much time to phytochemistry, discovering more than a score of important plant compounds besides those mentioned above. Other men followed in his footsteps and by the beginning of the last century many of the important plant compounds had been isolated.

At the very beginning of what may be justly called the renaissance in organic chemistry, Marggraf (1745–79) completed his historical work on the common beetroot. With his discovery and preparation of sucrose from the sugar-beet began the first and perhaps the greatest and most highly technical industry of modern times. It was likewise during the close of this first epoch that Pelletier began his classical work on the alkaloids, resulting in the discovery of no less than twelve of the important ones, including quinine, strychnine and brucine. In fact, it was during this same epoch that nearly all of the great families of plants were studied from the chemical point of view, resulting, in almost every case, in important discoveries. Even the resins, which chemists have until recently regarded as too complex to deserve serious attention, were studied in an industrial way and more than thirty different varieties prepared and used in the arts. But the resins were only one of the many groups of organic compounds regarded as too complex to admit of other than a study in the most general way, for organic chemistry had not advanced far enough to permit of a thorough chemical study of even the simplest of the organic substances. The adoption of the radical and the ring theories about the middle of the last century, however, completely changed the sphere of organic chemistry and synthetic methods and the chemical constitution of organic compounds became the goal toward which a large majority of chemists worked.

The adoption of the benzene ring theory, together with the working out of the chemical constitution of naphthalene, pyridine, quinoline and the terpenes, opened new fields in phytochemistry, and the first ten years of labor after the adoption of these new theories showed amazing results.

Structural and synthetic work in plant chemistry really began in the sixties. In 1869, Lieberman startled the whole chemical world by synthesizing alizarine, an important vegetable dye-stuff, and shortly after the alizarine synthesis, Baeyer succeeded in building up the indigo molecule.

Following these historical discoveries came numerous phytochemical syntheses, one of the most important being the artificial preparation of vanillin. Until Tiemann had shown that vanillin can be made cheaper in the laboratory than it can possibly be obtained from the vanilla plant, chemists, on the whole, were somewhat skeptical about the practicability of synthetic methods and especially as to the possibility of these synthetic compounds supplanting those produced by nature. The vanillin and the indigo syntheses, however, completely changed the whole chemical world in this respect. Men began to imitate nature in the building up of not only the vegetable, but also the simple animal compounds—a few enthusiasts casting longing glances at the constitutional formulæ of sugar, starch and cellulose, while the ultrachemical investigators dared even to speak in undertones of the structure of the albumins and the resins. Then came Baeyer's marvelous work on mellitic acid. His exhaustive study of this acid, which began as early as 1867, was so far reaching in its application to the ring compounds that it had much to do with final working out of the structural constitution of the terpene group.

There is a universal feeling, I think, among those who have watched the development of organic chemistry during the last twenty years, and especially along phytochemical lines, that in the not distant future all of the more important plant compounds will have been products of the laboratory. That there is ground for such a statement is borne out by what has already been done. The investigations of Loew, Butleroff, Kiliani, Emil Fischer and Wohl on the carbohydrates are so familiar to every one that it is only necessary to briefly refer to them at this time. The aldehyde condensation reaction by Loew and Butleroff, the building up of the sugars by Kiliani and the down-building by Wohl make the synthesis of the hexoses an established fact and the synthesis of the bioses at least a possibility in the near future.

The briefest phyto-synthetic review would be incomplete without referring to the most recent work of Emil Fischer and his pupils on the so-called polypeptides. Here is a group of complex substances belonging to the albumins of both the plant and the animal world, a group of compounds whose synthesis has, until recently, been regarded by many as beyond human possibility. Nevertheless, Fischer has built up the complex polypeptides until the artificial molecules are equal in size to the albumins themselves, leaving the synthesis of these complex chemical substances no longer in the list of vain possibilities.

Of scarcely less importance in the phytochemical world than the carbohydrates, the alkaloids and the albumins, are the resins and terpenes. Wallach has presented a satisfactory constitutional formula for pinene, but the resins are still classed with substances of unknown constitution. Notwithstanding the fact that less is known concerning the chemical nature of the resins than perhaps any other group of organic compounds, they are doubtless the oldest organic compounds known to man. They played an important part in the chemical industries in the early history of mankind. They were used in almost every phase of early human life, as lacs, varnishes, balsams, perfumes, pomades and in the art of embalming. They were described by the early alchemists as substances insoluble in water, generally soluble in alcohol, and for the most part non-crystallizable. They are the result of secretive plant fluids, exuding from plants and hardening in the air. They could not be separated into their constituents by any means known to the early chemists, and were therefore regarded as single substances. As a rule, however, they are mixtures of two or more complex substances, a gum and some volatile oil or terpene. They were known as gum resins or natural balsams and with the terpenes as oleoresins. As a result of their non-crystalline nature they were generally excluded from the list of substances worthy of investigation.

That there is a close chemical relationship between the resins and the terpenes, there can be no doubt, notwithstanding the fact that there is comparatively little experimental evidence to prove the assertion. One of the reasons usually given for the assumption is based on the fact that the resins and terpenes generally occur together in plants. This is by no means important evidence, for it frequently happens that entirely different groups of organic compounds are intimately associated with each other in both plant and animal life.

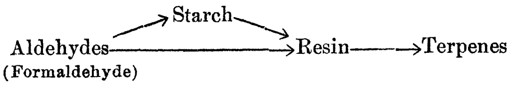
Notwithstanding the fact that considerable general industrial work has been done on the resins, especially those of the pine family, yet no one has been able to determine with certainty the molecular constitution of any of them, not even of abietic acid, the most common and the most important of all of the resin acids. Not only are the structural formulæ unknown, but in most cases the empirical formulæ are still in doubt. For instance, the formula for abietic acid has been generally accepted as $C_{20}H_{30}O_2$, but Mach in his dissertation on the acid gave to it the formula $C_{19}H_{28}O_2$. Absolutely nothing is known of its chemical constitution.

Various theories have been advanced concerning the relationship between the resins and terpenes. What evidence there is may be briefly stated. The fact that the aldehydes in the presence of alkalies change to resinous matter was presented by Wiesner in what may be called the reduction theory. Wiesner[2] assumed that the resins are formed from the carbohydrates, or, speaking more specifically, from the starches by a process of polymerization and reduction. It is perfectly evident that Wiesner's theory is not applicable in all cases. The pine family, for instance, contains a minimum amount of starch, yet it is the richest of the resinous species. Wiesner was aware of this fact and assumed that in the case of the pine family the resins were formed through the action of gallic and gallo-tannic acids.

While the starch theory has certain facts in its favor, there are, on the contrary, serious objections to it. It would seem not only strange, but also diametrically opposed to general chemical laws, that plants should proceed to build up the complex starch molecule and then break it down again into the resin and finally into the terpene molecule. Of course, it must not be forgotten that the sugars belong to the aldehydes and tend to form resinous substances when treated with alkalies. They are, however, by no means as readily converted into the resins as the simpler aldehydes. One would naturally expect that if the resins are formed by the aldehyde reaction they would proceed from the simple rather than from the complex aldehydes or sugars.

One of the first comprehensive works on the formation of the resins from the aldehydes was presented by Baeyer. He obtained several synthetic resins by the aldehyde condensation reaction, but an examination showed that they were unlike any of the resins found in nature. In each case the molecule seemed to be extremely complex and no attempts were made to determine the structure or the size of the molecule. Kronstein, following out the work which Baeyer had begun, presented constitutional formulæ for these aldehyde resins in a very unique but entirely empirical way. He assumed the resin molecule to be a complex benzene ring or perhaps several superimposed rings joined with either hydrocarbon, methoxyl, ethoxyl or carboxyl radicles, and gave the graphic formulæ for them. Of course such structural formulæ are interesting, but needless to say they are not based on experimental data.

In the starch explanations of the formation of the resins in plants, it must be assumed that the resins are formed by first building up the complex starch molecules from the simpler aldehydes, and then breaking them down again into the resins and terpenes. So far as can be ascertained there are no experimental data in favor of this theory. If, on the contrary, we assume that the resins are built up from the simple aldehydes, the process is more logical, as it only requires two steps, namely, polymerization and reduction, instead of three distinct steps as indicated in the following simple diagram:



While the above theories have many points in their favor, there is another

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[2] *Centr.*, 1865, p. 756.

which, while it may have some objections, has at the same time decided advantages over the starch or reduction theory.

It is common knowledge that the terpenes, when exposed to air, slowly change to complex polymers and resins of unknown composition. The principle involved is doubtless condensation followed by oxidation. Wöhler was the first to suggest that the resins may be built from the terpenes by the above-mentioned condensation and oxidation process. He based his assumption on the well-known fact that turpentine absorbs oxygen, forming a resin. This oxidation process may be represented by the following equation:

$$2C_{10}H_{16} + 3O = C_{20}H_{30}O_2 + H_2O.$$

Wöhler, unfortunately, presented no experimental data. Later, Cailliots obtained a resin by the oxidation of turpentine with nitric acid. It was not well defined, however, and not identical with any of the common resins, although it bore some semblance of common pine resin.

Barth[3] obtained, by oxidizing oil of lavender, a terpene, an amorphous resin which he carefully studied and gave the formula $C_{20}H_{30}O_3$, apparently an oxyabietic acid.

Heldt,[4] in an exhaustive study of the resins, produced common sylvic acid by oxidizing a polymerized form of turpentine according to the following equation:

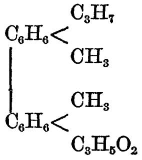
$$2(C_{10}H_{16}) \text{ or } C_{20}H_{32} + O_2 = C_{20}H_{32}O_2, \text{ sylvic acid,}$$

and

$$C_{20}H_{32}O_2 + O = C_{20}H_{30}O_2 + H_2O, \text{ or abietic acid.}$$

This work has been repeated, but without obtaining either sylvic or abietic acids.

One of the most interesting communications along this line was presented by Bruylaut. He obtained, by a method not given, a polymer of pinene which he represented as a condensation of two molecules of pinene or dipinene. By oxidizing this substance he obtained an acid which had the empirical formula for abietic acid:



No details of the work, however, were given.

Work on the condensation of the terpenes has been in progress at the University of Minnesota for several years. Before describing some of these experiments, however, it may be of interest to briefly trace the work on the synthesis of the terpenes themselves. It was observed early in this work that when pinacone is treated with bromine, an extremely complex reaction takes place and among the products formed are isopropyl alcohol and substances belonging to the terpenes. It was found, however, on carefully studying the reaction, that Baeyer had already observed this fact, but had not followed out the reaction, doubtless on account of the extreme complexity of the reaction. If, however, we take into consideration these two substances, the reaction may be represented as follows:

$$6C_6H_{14}O_2 = 2C_3H_8O + 3C_{10}H_{16} + 10H_2O.$$

Some time previous to this work, Kondakow[5] in his work on angelic and tiglic acids obtained from them a hydrocarbon which proved to be a methyl derivative of crotonylene. It had the general formula for the hemiterpenes. From the description it seems quite likely that this hydrocarbon is related to the terpenes, for it has the formula $CH_3{=}C(CH_3){-}CH{=}CH_2$, which is

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[3] *Ann.*, 143–313.

[4] *Ann.*, 63–48.

[5] *Jour. of the Russ. Phys. Chem. Soc.*, 1891, I., 178.

identical with the hemiterpene, isoprene.[6] Now, angelic and tiglic acids are comparatively common in the plant world and if, as Kondakow states, these hydrocarbons are readily obtained from the acids, then it is possible that the hemiterpenes are formed in this way and by the condensation of two molecules of the hemiterpenes, a terpene in this particular case, camphene, is formed according to the following simple equation:

$$2C_5H_8 = C_{10}H_{16}.$$

In pursuing the work of the terpene polymerization, practically all of the methods in the terpene literature were tried. All of them, however, were unsatisfactory. It was noticed in previous work on the chlorhydrochlorides[7] of terpenes, that in the preparation of the hydrochloride on a large scale there was always left a considerable portion of material of thick oil consistency after the chloride had been removed. Examination showed that this oil contained a small quantity of resinous matter. After unsatisfactory attempts to isolate the resin, other agents were tried. Bromine and iodine were tried and each was found to produce resins more readily than chlorine. As iodine gave best results, it was used in the experimental work which follows. It was found, first of all, that iodides somewhat similar to the chlorhydrochlorides could be formed, especially if the reaction took place in sunlight. These iodides were first isolated and studied. The diiodide proved to be of special interest. When pure it is a heavy colorless oil with a slight camphoraceous odor. When exposed to sunlight it readily decomposes, liberating iodine and resins, notwithstanding the fact that sunlight seems to play an important part in its formation. If exposed to sunlight for some time the iodine is all liberated and there is left a resinous mass composed chiefly of two substances. This resinous mass was subjected to distillation in vacuo. The distillate obtained was a thick, colorless, stable oil. Its molecular weight indicated a dipinene. It contained no iodine, and from its remarkable stability it is probable that the pinene radicles are doubly joined to each other. By oxidation it forms an acid isomeric with abietic acid. The residue left in the flask after the dipinene had been removed was also of unusual interest. It proved to be a solid of a light amber color. It had exactly the same melting point of ordinary rosin. Most of its properties were also identical with those of common rosin. It proved to be a tetra pinene, and, owing to its close resemblance to ordinary colophonium, it has been called colophonene.

These two condensed forms, the di- and the tetra-pinene compounds, have been isolated and carefully studied. Both are stable, but may be oxidized to acids with many of the characteristics of the resin acids. A comparison of these synthetic compounds with the natural resins is both interesting and important. Those which have been prepared and examined at the present time do not agree in every respect with the natural resin acids. This fact is not surprising, however, as any one of the different groups, occurring in the molecule when oxidized, would give a different acid. It would, therefore, be mere chance if the synthetic compounds should be identical with the common resin acid.

In summing up the experimental evidence in connection with the theories of the formation of the resins and terpenes and their chemical relationship, the following syntheses may, under different conditions, represent what takes place in certain phases of plant life:

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[6] It may be interesting to the reader to note that isoprene has very recently been polymerized to india rubber.

[7] *Jour. Am. Chem. Soc.*, 28, p. 1461.

1. The formation of the resins from the simple aldehydes.
2. The formation of the resins from the complex aldehydes or carbohydrates.
3. The formation of the resins from the terpenes.

It is not impossible that the resins are formed by any one of the above syntheses. There are abundant reasons for believing, however, that the synthesis of many of the resins is intimately related to the terpenes, that is, the terpenes may be first formed from simple compounds as the hemiterpenes, then converted into the resins by condensation and oxidation. This reaction seems entirely in accord with the chemical changes which naturally take place as phytochemical changes usually proceed from the simple to the more complex, as for example, from formaldehyde to the carbohydrates, but never from the carbohydrates to formaldehyde.

From the study of these terpene derivatives, it seems more than probable that the resins, at least those on the pine family, bear the same general relationship to the terpenes that naphthalene does to benzene and that the terpene molecule, $C_{10}H_{16}$, is the common substance from which the resins are derived.

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THE METAPHOR IN SCIENCE

THERE are several examples in the history of science where an idea at first represented by some metaphorical expression became in course of time a concrete existence. Most of the sciences have instances of it; one meets first with a notion, often of the vaguest, a principle, a property, a potentiality for something or other, and one ends with a substance, a species of matter, tangible and ponderable: the notion has become incarnated.

Inorganic chemistry offers us an excellent case of this sort of thing. When Lavoisier was working out the character of the substance we now know as oxygen, he had not isolated oxygen by a stroke of genius and then proceeded to study the properties of the new chemical product; the history of its discovery was far otherwise. Acting on some hints given him in October, 1774, by Joseph Priestley, Lavoisier came upon what he soon named as the "principle of acids" or "the acidifying principle"; his words are (1777):

> I shall therefore designate dephlogisticated air, air eminently respirable, when in a state of combination or fixedness by the name of acidifying principle or if one prefers the same meaning in a Greek dress by that of *oxygine principle.*

Here it is a principle, something which combines with metals when they are calcined or burned in air; it is that something which to Lavoisier seemed essential in acids, that which produced acidity, the oxygine principle. In its later and more familiar form of oxygen, it is better etymologically. That which was a principle in 1777 was about 120 years afterwards a visible, tangible entity—the liquefied, steel-blue oxygen gas. The principle of 1777 by 1897 had become a substance; the metaphor had become an actuality.

Not all chemical concepts have been equally fortunate in leading to true and individual chemical substances: phlogiston, for instance, denoting, as it did, no reality, is the conception phlogiston still. The principle of heat, phlogiston, was supposed to leave a body when it was burned: the theory of Stahl asserted that heat was a thing, a thing which could depart from a body and leave it lighter than before when it was cold. Now this, as a conception, is sufficiently definite, but as it is not true in fact, phlogiston never materialized; it was never isolated from matter because it never existed in matter. Phlogiston was as barren a conception as "oxygine" was pregnant. To-day Priestley and Lavoisier could be presented with an ounce or so of the "oxygine" principle, but not a milligram of phlogiston could be extracted for Stahl, for oxygen is a substance, but heat is a mode of motion. Probably the most pregnant metaphor ever used in science was Harvey's as