

ice in the lower parts of fissures. The drip would then naturally run into the cave, and as long as the temperature of the cave was below freezing point would help to form cave ice.

But this theory does not take sufficiently into account surface thaws. Thury's theory is very good and true enough in many respects, but it does not go far enough. The observations of Professor Fugger, and especially those of Captain Trouillet, make certain the fact that ice begins to form in a cave as soon as the temperature of the cave has sunk below freezing point, whenever, from any cause, water gets into the cave. This will occur whenever there is a thaw outside at any time during the course of the winter; and it is probably entirely correct to assert that ice is formed intermittently in caves all through the winter months.

In conclusion, I wish to say that I look on this paper as in the nature of a *preliminary report* only. I have collected a great deal more information about ice caves, which I hope to publish before long. The whole subject is as yet by no means exhausted, and further observations may bring forth valuable results, and I wish I might now see American scientists give more attention to the ice caves of our own continent.

RECENT ADVANCES IN THE STUDY OF THE RESINS.*

BY HENRY TRIMBLE.

HISTORY.

The earliest knowledge of the resins was probably derived from frankincense and myrrh; it is possible, by certain paintings on the walls of the ancient temple of Dayr el Báhri, in Upper Egypt, to recognize that they were important articles of traffic seventeen centuries before Christ; they were associated with such important commodities as

* Abstract of a lecture delivered before the Franklin Institute, December 4, 1896.

gold, ivory and silver. Amber, likewise, was held in great esteem by the ancients, and its history can be traced back to the twelfth century B. C.

The Mosaic writings of the Bible make frequent reference to *incense*, the chief ingredient of which was frankincense or *olibanum*. Later, a number of other resins appear in history; mastic is mentioned as existing in the fourth century B. C.; Venice turpentine also became known about that time, and a number of the other secretion appeared then or earlier. Galbanum, mastic and several other resins were mentioned three centuries B. C. Dioscorides recorded a still larger number in the first century of the Christian era.

The use of such resins as frankincense, myrrh, galbanum and mastic, in the preparation of their incense by the ancient Israelites, went far towards establishing the value of these drugs and in stimulating the trade in them. Some of these resins are used as incense at the present time.

The electrical properties of the resins early attracted the attention of the human race, and it is merely necessary to recall the fact that the word electricity took its name from amber because of that property. Amber was, and still is, consumed in large quantities by the Mohammedans in their worship.

Another resin, which is of interest on account of its antiquity, is scammony. Theophrastus, in the third century B. C., was acquainted with it, and it has been held in high esteem ever since.

Asafoetida was also in high repute by the ancients; it was used as a condiment in the tenth century, and the more fetid the drug the better it was liked.

These few illustrations may serve the purpose of establishing the antiquity of the resins, and especially the fact that they were considered of the greatest value by the people of ancient days.

DISTRIBUTION OF THE RESINS.

The resins are so widely distributed throughout the vegetable kingdom that there is, perhaps, no plant but will

yield some resinous substance, either by secretion or by extraction with alcohol. All parts of the plant, too, yield one or more of these substances, with the exception of the cambium, which appears to be free from resinous constituent. As a rule, the bark contains resin most abundantly, although in a few cases, as in certain conifers like the larch and our Southern pines, the sap wood contains more, and appears to be capable of secreting it almost indefinitely.

The conifers of the present time, as well as those of a former epoch, have been the great producers of resins. Those in tropical and semi-tropical climates have been found to yield them most abundantly. Usually resins are associated in plants with volatile oils, and such exudations are frequently known as balsams.

A number of resins occur in nature, which are the product of trees and plants not existing at the present time; for example, amber is supposed to have originated from pines of the Miocene period. Copal is also found under conditions which indicate that it is not derived from the vegetation of to-day, with the exception, of course, of certain of the cheaper varieties. Much of the true copal gives evidence of having been under water for a long period. In the study of the resins, therefore, it will be seen that we are confronted with some of the most serious problems in geology, and, as our knowledge of the chemistry of these substances becomes more exact, we may be able to assist in answering some geological questions by their aid.

THE PHYSIOLOGY OF THE RESINS.

This subject is closely allied to the occurrence of the resins. It is a subject, however, on which at present we have very little light.

Botanists have investigated it with the aid of the microscope, and have, consequently, drawn conclusions at variance with those of chemists.

A number of the former have concluded that resins result from the destruction of cell walls, and are, therefore, the decomposition product of cellulose.

Wiesner* believed that the starch of the cell contents contributed to the formation of the resins, and that this was effected by the aid of a middle group, namely, the tannins.

Chemists, on the other hand, usually maintain that the resins originate from the terpenes, or from aldehydes.

It is difficult to accept the theory of their origin from starch when we consider that very little starch exists in some of the tissues which yield resin most abundantly, as in the long-leaf pine. That tannins have a close relation to the formation of resin is generally conceded. The following argument in support of this has been advanced by E. S. Bastin:† “It is pertinent to note in this connection that all the facts observed regarding the oleoresins of the pines show that they are very closely associated with the tannins. While this of itself does not prove that the former are derived from the latter, the nature of the association is such as to strongly suggest such a conclusion. For example, a secretion reservoir begins in a cluster of a few thin-walled cells, rich in granular protoplasm, which early shows an abundance of tannin. Later on, oleoresinous matters appear, and, as these increase in quantity, the tannin and the protoplasm diminish, and, finally, the walls break down, leaving a cavity or intercellular space containing the oleoresin. In the meantime, cells immediately bounding this space are gradually undergoing similar changes, and so on, as long as the secretion reservoir continues to grow. So, if any well-developed secretion reservoir with the surrounding cells be examined, there will be found:

“(1) A central space filled with oleoresin.

“(2) An area of cells immediately surrounding this, which contain much oleoresin, and a little tannin and protoplasm.

“(3) Still farther exterior, a layer of very granular cells, rich in protoplasm and tannin, but containing very little volatile oil or resin.

* *Sitzungsbericht, der k. Akad, zu Wien.*, Bd. 51; also “*Die Rohstoffe des Pflanzenreiches*,” p. 69.

† *Am. Jour. Pharm.*, 68, 137.

"There is no denying the fact that, as the resin increases, the tannin diminishes, whatever the conclusion we may draw from the circumstance.

"The view that tannins are derived from starch apparently obtains no support from these observations on the pines.

"In regard to the origin of resin from volatile oil, the microscopic study of the pines, especially of *Pinus palustris*, seems to afford pretty clear evidence in the affirmative. Old secretion reservoirs have been observed to contain irregular solid or semi-solid masses of oleoresin, in which, apparently, the resin is the predominating element, while young reservoirs contain a more fluid oleoresin in the form of globules. Moreover, in the secretion cells immediately surrounding the reservoirs, the oleoresin is in globules and evidently very fluid. In fact, in passing from the younger to the older portions of the secretion tissue, there appears to be every gradation between a very liquid volatile oil and a semi-solid resin.

"There appears to be no question that the oleoresin is to be regarded wholly as a waste product. It clearly can play no part in the process of nutrition. Its only apparent use is that of protection against the destructive forms of animal life and against vegetable parasites. It is highly antiseptic, it protects mechanically against injurious insects, and its taste and effects are disagreeable to most of the higher animals."

That the resinous secretion may, in certain conifers, be diverted, so as to be an entirely different substance, closely resembling the sugars in physical properties, is seen in the sweet secretion of the sugar pine, *Pinus Lambertiana*, of California. While this substance does not belong to the carbohydrates in a strictly chemical sense, still, it is as closely allied to them as is phenol to the alcohols of the paraffin series.

Why one pine should secrete sugar and its near neighbor, botanically and geographically, should secrete resin is a question wide open for speculation, as well as for exact botanical and chemical research. In a number of cases gums of the carbohydrate series are a part of the resinous secretion whereby we get the gum resins.

GENERAL PROPERTIES OF THE RESINS.

The resins, as a class, vary too much from one another to have many properties in common. There are, however, a few characters which have already been cited in defining them, and which belong to all of them. They are all insoluble in water, mostly amorphous, rarely opaque, being either transparent or translucent. When pure, they are odorless and tasteless, but as they are associated, in a number of instances, with volatile oils and aromatic acids, they often have an aromatic odor and a bitterish taste. They are mostly easily melted at 100° to 150° C., although the harder copals melt above 200° C. They are usually soluble in alcohol and turpentine, and many of them are dissolved by benzol, petroleum ether, carbon disulphide and the fixed oils. The resins neither decompose nor volatilize, and they may remain unchanged in the earth or under water for centuries. An illustration of their keeping qualities occurred in 1885, when a lot of benzoin was offered for sale in London that had been raised from a wreck off the southwest coast of Africa, which occurred in 1691. The resin was found to be of excellent quality, yielding 92 per cent. of its weight to alcohol, and containing more than the ordinary amount of benzoic acid. Presumably, it should have lost some of the latter constituent during its 200 years' sojourn at the bottom of the ocean.

CHEMICAL COMPOSITION.

With the chemistry of the resins is closely allied their classification. Their classification must eventually be a chemical one, if they retain their identity as a class. Liebig was satisfied with a separation into hard resins and soft resins. This classification had previously been adopted by Berzelius, although the latter also spoke of a classification which distinguished those resins which exuded from trees spontaneously, and those which were extracted by alcohol.

About the same time, Unverdorben classified the resins according to their behavior towards ammonia. This investigator's classification is sometimes referred to by writers of the present day, but the only value it has now is historical.

He did establish a number of the properties possessed by the resins, especially their behavior towards alkalies and some metallic salts ; also the electrical properties of a number of them. It may be remarked here, however, that in "Lavoisier's Chemistry" (1806) is a short account of the behavior of resins towards alkalies, and the statement is briefly made that "with alkalies it forms soap, and is much used in manufacture for that purpose, being a chief ingredient in yellow soap, and that to which it owes its solidity."

While the edition from which this quotation was taken was issued some time after the author's death, still the property of resin to form soap was, no doubt, known much earlier.

Hirschon,* in 1878, published a "scheme for the recognition of the more important resins, gum resins and balsams. While this is of considerable value analytically, it does not add to our knowledge of the chemical composition of these bodies.

We find in the text-books of to-day a nomenclature of the resins which stands in the way of a clear comprehension of their composition and properties. For instance, benzoin is said to consist of α , β , γ and δ resins, a conclusion of over half a century ago, based on the action of certain solvents. The analysis on which such a statement is based was published in *Liebig's Annalen* in 1840, and looks something like the following :

	Per Cent.
Benzoic acid	3'00 to 14'5
α resin	3'0 to 3'5
β resin	52'0 to 48'0
γ resin	25'0 to 28'0
δ resin	0'8 to 0'5
Foreign matter	5'2 to 5'5

Hlasiwetz,† in 1867, contributed a paper on the relations of the tannins, glucosides, phlobaphenes and resins with one another, and both he and Rochleder added considerably

* *Pharm. Zeit. für Russland*, **16**, 81, and *Am. Jour. Pharm.*, **50**, 130.

† Ueber die Beziehungen der Gerbsäuren, Glucoside, Phlobaphene und Harze. Von H. Hlasiwetz, *Sitzungsberichte der math.-naturw. Classe* **55**, (II), p. 575.

to our knowledge of the various resins, although no comprehensive system of classification was accomplished.

Flückiger also added much to the knowledge of individual resins, especially in reference to their history and sources.

This brings us down to the present time ; and during the summer just passed Professor Tschirch, of Berne, Switzerland, has published a classification based on a study of individual resins, by himself and his students, which investigation has been progressing for a number of years. It is to be hoped that this work will be continued, for the results on the individual members of the class thus far investigated point in the direction of simplicity.

Copal, dammar, sandarac, dragon's blood, asafoetida, galbanum, ammoniac, sagapenum, opoponax, acaroid, benzoin, tolu, balsam peru, the fruit of liquid amber, storax, amber and gutta-percha have been investigated, and the following bodies have been found as the chief constituents :

- (1) Resin esters, or their derivatives.
- (2) Resin acids (resinolacids).
- (3) Resenes, indifferent bodies of unknown origin.

Only very few of the resins contain members of all three groups. Much oftener they consist of only one member of the group.

The odor, when present, is due to ethereal oil or aldehyde, or, oftener, to a very small quantity of an ester of cinnamic acid, especially the phenyl-propyl ester of that acid.

I. The resin esters, or those containing aromatic acids are divided into two classes. One consists of compounds with benzoic acid, and the other with cinnamic acid.

(1) Benzoic ester is contained in balsam peru, balsam tolu, siam benzoin and dragon's blood. Ammoniac contains an ester of salicylic acid. Benzoyl acetic acid is contained in dragon's blood.

(2) Cinnamic ester is contained in balsam peru, balsam tolu, storax, sumatra benzoin, yellow acaroid.

An ester of cumaric acid is contained in yellow and red acaroid resin.

An ester of ferulic acid is contained in asafoetida.

Umbelliferic acid and its anhydride, umbelliferon, exist in combination in asafoetida, galbanum and sagapenum.

Most of the aromatic acids forming esters in resins are oxy-acids.

The only acid of the fatty series forming a resinous ester is succinic acid in amber.

The resin esters contain resin alcohols, which are either colorless and do not give the tannin reaction, or are colored and give the tannin reaction. The former are called *resinols*, the latter *resinotannoles*.

(a) Resinols.—Of these, four are known :

Succinoresinol,	$C_{12}H_{20}O$, in amber.
Storesinol,	$C_{12}H_{20}O$, or $C_{36}H_{58}O_3$, in storax.
Benzoresinol,	$C_{16}H_{25}(OH)O$, in benzoin.
Thirinol,	$C_{28}H_{47}OH$, in opoponax.

Spectrum analysis of their solutions in concentrated sulphuric acid shows storesinol and benzoresinol to be closely related. Succinoresinol and storesinol have the same percentage composition. All the members of the resinol group are related among themselves, and all belong to the aromatic series.

(b) Resinotannoles.—The following are known :

Siaresinotannol,	$C_{17}H_{13}O_2 \cdot OH$, in siambenzoin.
Sumaresinotannol,	$C_{48}H_{19}O_3 \cdot OH$, in sumatrabenzoïn.
Peruresinotannol,	$C_{18}H_{10}O_4 \cdot OH$, in peru balsam.
Toluresinotannol,	$C_{17}H_{17}O_4 \cdot OH$, in tolu balsam.
Galbaresinotannol,	$C_{18}H_{29}O_2 \cdot OH$, in galbanum.
Ammonoiresinotannol,	$C_{18}H_{29}O_2 \cdot OH$, in ammoniacum.
Sagaresinotannol,	$C_{24}H_{27}O_4 \cdot OH$, in sagapenum.
Dracoresinotannol,	$C_8H_9O \cdot OH$, in dragon's blood.
Ponaxresinotannol,	$C_{34}H_{40}O_7 \cdot OH$, in opoponax.
Xanthoresinotannol,	$C_{43}H_{46}O_{10}$, in yellow acaroid.
Erythroresinotannol,	$C_{40}H_{40}O_{10}$, in red acaroid.

Six of these show a multiple of six carbon atoms.

In many other ways there is a close relationship among the various resinotannoles.

It is evident that the resinotannoles contain but one hydroxyl group in the molecule.

The ready formation of picric acid by treatment of the resinotannoles with nitric acid leads us to believe that the

hydroxyl is attached to the benzol nucleus, and not to a side chain. On fusing with alkali hydrate fatty acids are formed; in some cases, protocatechuic acid or resorcin is produced. The resinotannoles belong to the aromatic series.

II. The resin acids exist in the resins in the free state; they are, so far as investigated, oxy-acids, that is, contain hydroxyl and carboxyl. The following have been separated and investigated:

Podocarpinic acid,	$C_{17}H_{22}O_3$, in podocarpus resin.
Abietinic acid,	$C_{44}H_{64}O_5$, in colophony.
Pimaric acid,	$C_{20}H_{30}O_2$, in pine resin.
Succinoabietinic acid,	$C_{80}H_{120}O_5$, in amber.
Sandaracolic acid,	$C_{43}H_{66}O_7$, in sandarac.
Callitrolic acid,	$C_{65}H_{84}O_8$, in sandarac.
Trachylolic acid,	$C_{56}H_{86}O_8$, in copal.
Isotrachylolic acid,	$C_{56}H_{86}O_8$, in copal.
Dammarolic acid,	$C_{56}H_{80}O_8$, in dammar.
Guaiacic acid,	$C_{20}H_{26}O_4$, in guaiac.
Guaiaconic acid,	$C_{19}H_{20}O_5$, in guaiac.
Copaivic acid,	$C_{20}H_{30}O_2$, in copaiva.

Many of these resins are found to be related to one another.

III. The most difficult class of resins is, without doubt, the *resenes*. Their resistance to reagents has given them the synonym of indifferent material, and has made them difficult to classify. They are neither hydrocarbons, alcohols, esters, acids, ketones or aldehydes, but belong, so far as investigated, to the aromatic series.

The following have been examined:

α ponaxresen,	$C_{32}H_{54}O_4$, in opoponax.
β ponaxresen,	$C_{32}H_{52}O_5$, in opoponax.
α dammarresen,	$C_{37}H_{52}O_3$, in dammar.
β dammarresen,	$C_{31}H_{52}O$, in dammar.
Fluavil,	$C_{40}H_{64}O_4$, in gutta-percha.
Alban,	$C_{40}H_{64}O_2$, in gutta-percha.
α copalresen,	$C_{25}H_{38}O_4$, in copal.
Dracoalban,	$C_{20}H_{40}O_4$, in dragon's blood.
Dracoresen,	$C_{26}H_{44}O_2$, in dragon's blood.
Myroxoresen,	$C_7H_{10}O$, in myroxylon fruit.

When the formulas of these are carefully studied they are found to have some relation among themselves.

If it be asked what is the practical value of a classifica-

tion like this? the answer may be found in the present knowledge of benzoin compared with what it was a few years ago, when this resin was said to consist of benzoic acid and alpha, beta, gamma and delta resins. At the present time we know that this resin is a compound of benzoic acid with benzoiresenol, and a compound of resinotannol, the latter varying somewhat in the different varieties.

Further than stating that the resinotannoies are peculiar compounds or mixtures of tannins and resins, we cannot at present go, except that they contain one hydroxyl group and appear to have a multiple of six carbon atoms. Certainly the chances of discovering the secret of the chemical constitution of these bodies by this road are very materially advanced, even if the task does appear somewhat formidable.

GRAPHICAL DETERMINATION OF THE INDEX OF
THE POWER ACCORDING TO WHICH ONE
QUANTITY VARIES RELATIVE
TO ANOTHER.

BY PROF. W. F. DURAND.

It often happens in engineering investigations that a curve is found expressing the simultaneous relationship between two quantities; for example, an indicator diagram showing the relation in the cylinder between pressure and volume; or a diagram showing the relation between engine economy and point of cut-off or load; or between the resistance or power of a ship and her speed; or between the head of water-pressure on an orifice and the velocity or amount of efflux; or between the work required to remove a lathe chip and the depth or speed of cut, etc.

Now, with all such curves it is frequently desirable to determine the instantaneous index of the power according to which one of these quantities varies relative to the other. We may thus say that at a certain point in the stroke of a steam engine, the pressure, according to the diagram, varies inversely as the n th power of the volume; that is, at that