THE RELATION BETWEEN TAXONOMY AND CHEMISTRY OF PLANTS

by

TH. WEEVERS.

(Plant-physiological Laboratory, University of Amsterdam).

The first question in this field of science is: can we say, that there is actually any relation between taxonomy and chemistry of plants? Nearly a century ago the worker in chemistry Rochleder (10) attempted to show the possibility of this relation and called that branch of science phytochemistry.

To begin with, something must be said about the products in question. Glucose, sucrose, several aminoacids and other acids are, of course, left out of account. Only those chemical products, which are more or less specific and characterise larger or smaller groups of plants are considered here.

Is there really any relation between the chemical nature of these products and the taxonomical position of the plant by which they are formed? This is not a matter of course; since Linnaeus constructed his first so-called natural system, the systems were always based upon comparison and valuation of morphological characteristics: form and construction of different organs, especially those which are concerned with sexual propagation.

In the taxonomy of the Cryptogams some morphological characteristics are used, which can easily be transferred into chemical ones. A classification in Bluegreen, Red, and Brown Algae, which still has its right of existence, only means the formation of certain coloured chemical products. The classification of the Cormophytes however, seems at first sight to show not the least relation between chemistry and taxonomy; only form and structure are decisive here. Although historically explainable this is rather illogical.

Form and structure are, as it were, a function of a higher order than the formation of chemical products but they are founded on properties, which possess the closest connection with metabolism.

Workers in this field of science who, following the track of Rochleder, lay stress upon this connection of chemistry and taxonomy, are not rare. One of them is the Russian botanist Sergius Ivanow (3) who in the year 1926 gave us his so-called biochemical laws, which may be briefly formulated as follows:

1°. Each species growing under the influence of normal external factors is able to produce its characteristic products, which Ivanow calls the physiological characteristics of this species.

2°. Each species has these physiological characteristics in common with the species, which are in genetical connection with it.
3°. If this connection is more distant new products arise, which have a simple chemical relation with the basal products from which they originated.
4°. These physiological characteristics are liable to evolution.

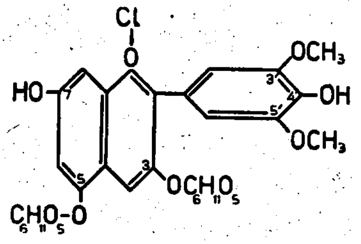
In my opinion it is incorrect to call a chemical product a physiological characteristic; the ability to form the product may be regarded as such. Setting this aside, the question remains whether these laws of Ivanow are correct or not.

Two ways are open to put these laws to the test: the first is to consider whatever genetics teach us about the chemistry of newly originating mutations and their crosses with the mother-species. A second way is offered by a careful comparison of the chemistry of higher plants, especially in relation to their place in the botanical system.

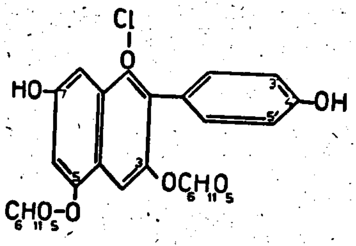
As to the first point, data are almost entirely lacking; although genetics has often studied loss or formation of a chemical product, usually a coloured one, the chemical nature of these products in detail has rarely been taken into consideration. A happy exception, however, is formed by a group of English workers, who attempt to link up pigment chemistry with information on genetic factors, controlling colour variations in higher plants.

From a paper by Rose Scott Moncrieff (11) I cite some particulars about changes in the chemistry of flower pigments, observed in mutations of *Lathyrus odoratus, Primula sinensis* and *Rosa Polyantha.*

LATHYRUS ODORATUS



Malvidin 3.5' dimonoside



Pelargonidin 3.5' dimonoside

Fig. 1.

Anthocyanins are glycosides, formed by the combinations of one or two molecules of hexose or pentose with an aglycone called anthocyanidin. Variations in these anthocyanidins occur, owing to hydroxy- or oxymethyl-substitutions in the so-called side-phenylring. In the main form of *Lathyrus odoratus* e. g. one finds the malvidindimonoside with two hexose-molecules and with two OCH_3- and one OH-group in the side-phenylring. By mutation a peonidindimonoside originates, in which one OCH_3-group is lost. By further mutation in this direction the second OCH_3-group also disappears and pelargonidindimonoside is produced.

Rosa Polyantha gives an example of the contrary: from the main form, containing a pelargonidinrhamnoglycoside with only one OH-group, a mutation originates containing cyanidinrhamnoglycoside, which possesses two OH-groups in the side-phenylring.

The variations in the number of OCH_3- or OH-groups are interesting because similar differences exist between alkaloids in different species. The genus is characterised by a combination of alkaloids of one and the same type whilst the species of this genus have characteristic variations of this type, differing e. g. in the number of OCH_3- or OH-groups.

Greater chemical changes are to be found in plants with volatile oils: e. g. *Thymus Serpyllum* is characterised by a mixture of volatile oils with the benzenederivatives thymol or cymene as principal product, whilst *Thymus Serpyllum* var. *citriodora* contains volatile oil in which the aliphatic terpene citral dominates.

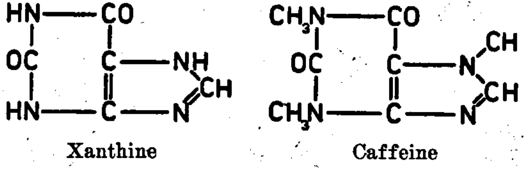
The above mentioned facts consequently show a close connection between the chemistry of a species and its genetical constitution.

Considering the question from another point of view we can pay attention to the chemical products in the subdivisions of the Cormophytes. We are then struck by the following: in mosses alkaloids, glycosides and volatile oils (from special glandular cells) are lacking; in Vascular Cryptogams alkaloids and glycosides are also lacking, whilst volatile oils may be present. Considering the situation in seedplants we note the presence of volatile oils and glycosides in Gymnosperms, whilst alkaloids are almost entirely lacking here. In Angiosperms however these three groups of chemical compounds are widely distributed, but in Sympetals their presence is more general than in the other groups. Generally speaking, the higher the place in the taxonomical system, the more complicated the chemistry.

American workers, especially McNair (7) tried to work out this problem and to use the chemistry of the species as an indicator of the place which species and genera containing these products occupy in the system. Underneath I hope to explain his methods more in detail.

Now the question arises: Are there no objections to the biochemical laws of Ivanow? Indeed there are: besides products which are formed everywhere in metabolism there are on the one hand a great number of chemical compounds which are only to be found in one single group of species and may be said to typify it. On the other hand, however, a small number of products exists, which are likewise present in several genera, but in genera of a completely different morphological structure and belonging to quite different parts of the tribe of Angiosperms. As an example of these compounds I may cite the alkaloid caffeine, the indigo-glycoside indicoside and the aromatic product eugenol.

Caffeine is to be found in *Centrospermae, Columniferae, Gruinales, Parietales* and *Rubiales*, in each case in one single genus or in only some species of one genus.



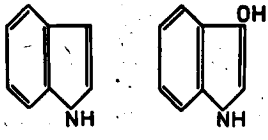
Xanthine Caffeine

Fig. 2.

Indicoside is present in some species of the *Polygonales, Rhoeadales, Leguminosae, Contortae* and *Synandrae*, whilst eugenol is met with in e. g. *Coniferae, Myrtales, Gruinales (Burseraceae), Tubiflorae (Labiatae)* and *Scitamineae*, again in one single genus or some species of it.

It is evident, that this fact is contrary to the biochemical laws of Ivanow and at the same time it seems to be a decisive argument against the considerations of phytochemistry, which so closely connect the chemistry of a species with its place in taxonomy.

Do these products as caffeine, indicoside and eugenol possess pecularities which distinguish them from the chemical compounds characteristic for a single and strictly limited group? This, indeed, is the case and the difference is that the former have a close connection with ubiquitous metabolic products.

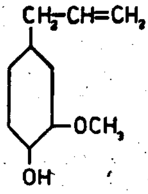


Indol Indoxyl

Fig. 3.

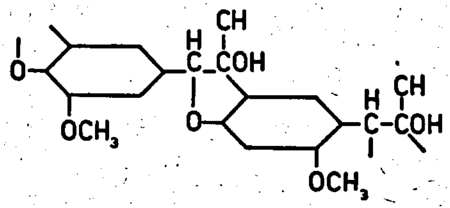
Caffeine or trimethylxanthine is closely connected with xanthine itself and the latter is an ubiquitous product of nucleoproteidmetabolism.

The aglycone of indicoside is indoxyl, which has a close connection with indol and tryptophane, both products of protein metabolism.



Eugenol

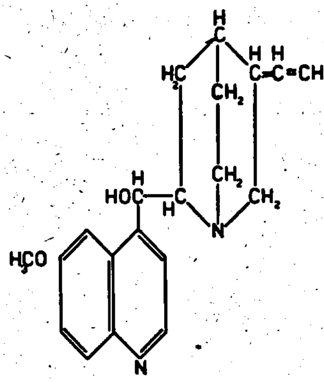
Fig. 4.



Lignin

Fig. 5.

Eugenol may be connected with lignin (15), a compound which characterises lignified cellwalls. In the case of lignin I must remark, that such aromatic terpene compounds are only met with in those divisions of the vegetable kingdom, in which lignified cellwalls are present (Vascular Cryptogams and Spermatophytes). Moreover the formation of such glandular products always takes place in connection with the cellwall (5).



Quinine

Fig. 6.

In contrast with the above mentioned products as caffeine c.s., which are closely connected with ubiquitous metaboles, this is not the case with compounds as strychnine or quinine, which characterise definite genera. It would lead us too far, to treat this in detail, but a glance at the formula of quinine makes it clear. Quinine can only be built up by a series of mutations, whilst a product as caffeine with its wide dispersion in the Angiosperms may have originated from an ubiquitous metabole by one single mutation.

It is evident, that one single mutation may have taken place more than once and in different parts of the genealogical tree, whilst it may be called exceedingly improbable that the same series of mutations should repeat itself twice.

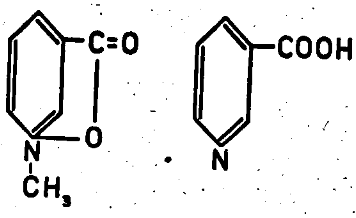

Trigonelline Nicotinic acid

Fig. 7.

One fact seemed to militate against the hypothesis that those alkaloids, which are most widespread, ought to be the most easily derived from generally occurring products of protein metabolism, i. e. that trigonelline is the alkaloid of the most widespread occurrence [1]), as this is the betaine of nicotinic acid or pyridino-carbonic acid and neither this nor pyridine itself were known to be common products of metabolism.

Experiments however of Warburg, Christian and Griesen (14) have come to prove that the coferment of dehydrases is an amido-derivative of pyridine, which through hydrolysis yields nicotinic acid, in which connection it should be remembered that trigonelline as I have already said above, is the betaine of nicotinic acid. As cozymase is also a nucleotide containing nicotinic acid, we may say that trigonelline can be derived in a straightforward way from a common product of metabolism.

The conclusion is, that the laws of Ivanow are not valid for compounds which have a close connection with ubiquitous products; in other words, these compounds are not typical for the taxonomical position of the species containing them.

More may be said about the fundamental facts of phytochemistry but for this it is necessary to enter somewhat more into detail as to the methods of taxonomy in classifying species. Usually not a single characteristic but a combination of them is taken into consideration. To be fair the same treatment ought to be followed in considering the

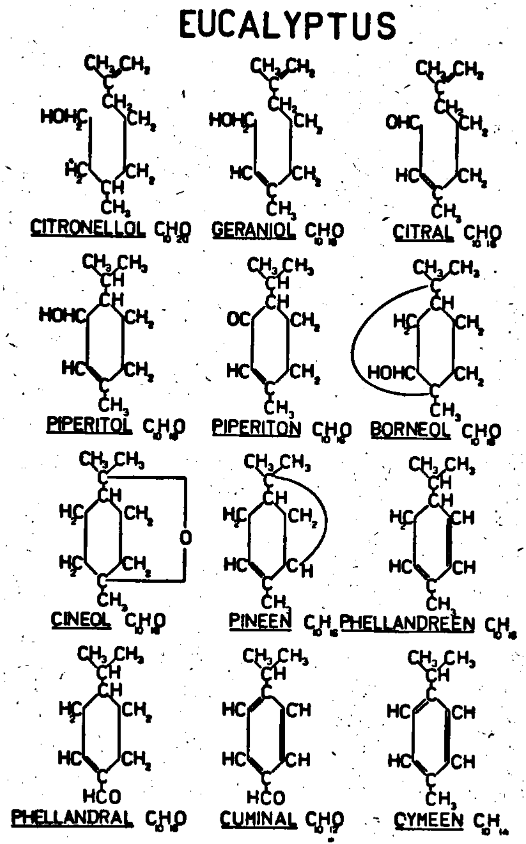


Fig. 8 — Note. For piperiton, pineen, phellandreen, cymeen, read: piperitone, pinene, phellandrene, cymene respectively.

---

[1]) Trigononelline is found in 18 different families, caffeine, the next alkaloid for widespread frequency, in only 6 families.

taxonomical value of chemical compounds. Not one single product but a combination of products has often to be used as a characteristic (16).

In doing this we note, that at one blow everything has changed. Cineol e. g. is present in a number of approximately 40 families belonging to quite different branches of the Angiosperms: *Labiatae, Compositae, Myrtaceae, Zingiberaceae,* etc. but a definite combination of volatile oils with cineol as main constituent completely characterises the genus *Eucalyptus.* As appears from an accurate study by Baker and Smith (1) of the volatile oils of this large Australian genus, the combination of chemical compounds in detail is different in each species. This is due to the fact, that besides cineol the Eucalypts may contain pinene, phellandrene, geraniol, citral, cymene, terpinene etc., in all some 20 different compounds, variously combined.

The same may be said for the volatile oils of the genus *Pinus,* in which pinene is everywhere present.

The alkaloid protopine is met with in nearly all *Papaveraceae,* but each genus and perhaps each species has its own characteristic combination of alkaloids. These alkaloids are derived from the products of protein-metabolism tyrosine and dioxyphenylalanine and the same is the case with the alkaloids of several other groups of plants. But the alkaloids of the *Papaveraceae* are derived in a special way and are present in a combination which is nowhere else to be met with.

The combination of these alkaloids again differs in the different parts of the family. The *Fumaroideae* with their zygomorphic flowers and their stamens united into two bundles, present a combination of isochinoline derivatives different from the one which characterises the *Papaveroideae* with their actinomorphic flowers and free stamens. The genus *Corydalis* contains a combination with differs from that found in the genus *Fumaria.*

As a last example I cite the plants with the glycosides, notorious for their action on the heart, e. g. *Digitalis* spec. div. (*Scrophulariaceae*), *Strophantus (Apocynaceae), Adonis vernalis (Ranunculaceae), Convallaria majalis* and *Urginea Scilla (Liliaceae).*

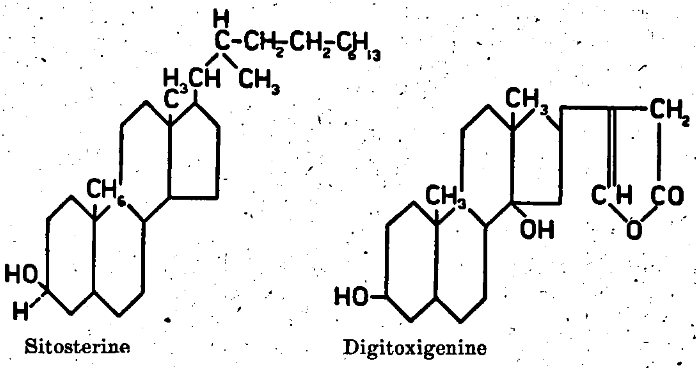
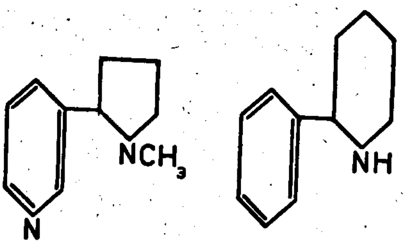


Fig. 9.

Of late years, our knowledge of these compounds has advanced enormously by the work of Windaus, Tschesche (13), Jacobs (4) and others; it has been found that these glycosides bear a great resemblance to each other as regards their chemical composition.

The aglycones digitoxigenine and gitoxigenine from *Digitalis,* and cymarigenin from *Strophantus,* are composed of 23 C-atoms and the structure proved to be a complex carbon-system of 3 six-rings, one five-ring and a lacton-ring. The structure bears a close resemblance to that of the sterines, compounds which seem to occur in every plant cell as well as in the animal cells. Still the structure in detail is different in each genus, often in each species. Not only the aglycones but also the carbohydrates which take part in the constitution of the natural glycosides may differ.

I might continue in this manner, but I prefer to treat some cases, which at first sight seem to tell against this phytochemical maxim, that each genus and perhaps each species has its own combination of chemical compounds.



Nicotine Anabasine

Fig. 10.

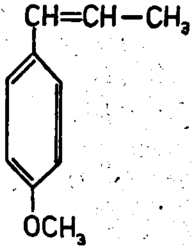
As for the alkaloids I take nicotine, which till lately was considered as typical for the genus *Nicotiana.*

From the species *Nicotiana Tabacum* the worker in chemistry Pictet (9) had isolated besides the main alkaloid nicotine a small number of so-called secondary alkaloids, which are present in very small quantities; in other genera this type of alkaloid was unknown. A few years ago, however, an alkaloid was isolated from *Anabasis aphylla,* a *Chenopodiaceae* from Asia Minor, whose chemical properties so much resembled those of nicotine, that at first sight they were supposed to be identical. Afterwards this proved to be incorrect; anabasine, the alkaloid from *Anabasis,* is built up by coupling two pyridine-rings, one hydrogenated, one not, whilst nicotine is built up by coupling a hydrogenated pyridine-ring with methylpyrrolidine. One of the secondary alkaloids of *Nicotiana Tabacum,* which is the main alkaloid in *Nicotiana glauca,* is, however, identical with anabasine (12). In these two quite different branches of the Angiosperms the same alkaloid is met with, the combination of alkaloids is, however, quite different; in *Anabasis* e. g. lupinine is found, an alkaloid which in *Nicotiana* is lacking.

A second example is taken from the glycosides: in the woods of the eastern part of the United States two species are met with from which the odoriferous compound methylsalicylate can be obtained. These species are: *Betula lenta,* a kind of birch, and the evergreen shrub *Gaultheria procumbens,* belonging to the *Ericaceae.* Both plants contain the glycoside gaultherin, which by enzymatic action of gaultherase gives methylsalicylate. Tracing the combination of typical products in both species it appears that in *Gaultheria procumbens* gaultherin is combined with the glycoside arbutin, which is typical of a great number of *Bicornes. Betula lenta,* on the other hand, contains no arbutin and whilst the volatile oil from *Gaultheria* is optically active, that from *Betula lenta* is optically inactive. Here too, at first sight a complete agreement in chemistry seemed to exist, whilst a further investigation showed us the incorrectness of it.

A third case is taken from plants with volatile oils: *Pimpinella Anisum,* belonging to the *Umbelliferae* takes its flavour and taste from the presence of the aromatic compound anethol, which is also met with in other *Umbelliferae* (note the resemblance of anethol to the formula of lignin), e. g. fennel, *Foeniculum vulgare.* Now this anethol is also the main ingredient of the volatile oil from the magnoliaceous *Illicium verum,* belonging to quite another part of the Angiosperms. By examination of the products, which are present in both plants besides anethol, it is proved that the combinations are quite different: star anise, *Illicium verum,* contains traces of terpenes, which are lacking in the common anise.

It is interesting to study in this respect the behaviour of caffeine a compound whose dispersion in the vegetable kingdom was quoted above as an argument against the laws of Ivanow. Is even this compound present in different combinations in the genera containing it? The question must be answered in the affirmative:



Anethol

Fig. 11.

1°. *Coffea* (*Rubiaceae*): caffeine main alkaloid, trigonelline secondary alkaloid;

2°. *Thea* (*Ternstroemiaceae*): caffeine main alkaloid, theophylline, theobromine and monomethylxanthine secondary alkaloids;

3°. *Cola* and *Theobroma Cacao* (*Sterculiaceae*): theobromine main alkaloid in the latter, caffeine secondary alkaloid, whilst in *Cola* the reverse is the case;

4°. *Ilex* (*Aquifoliaceae*): only caffeine present in some species of this genus;

5°. *Paullinia* (*Sapindaceae*): caffeine main alkaloid in the seeds, theobromine in the leaves.

Even if we only pay attention to the alkaloids, the combination is different in the genera containing these xanthine derivatives.

In short, each genus, often each species has its specific combination of these chemical compounds. A classification along these lines is often analogous to the usual classification on a morphological base.

The objection might be made, that a number of families exist in which no alkaloids or glycosides are present. Volatile oils have a much wider dispersion: even in plants in which glandular cells are lacking, compounds are produced, which give flavour to plants or flowers. Smell and taste, senses which are practically incapable of analysis but possess an acute perception of the whole, often notice small differences by which one species is distinguished from the other. Consider the scent of flowers, often insufficiently analysed in chemical respect, but so characteristic for a species. Consider the difference in taste and smell of our vegetables;

even varieties of the species *Brassica oleracea*, possess obvious differences, besides much they have in common.

And still there are products which have been left out of consideration and which are probably nevertheless the most characteristic ones, viz. the proteids.

The difficulty is, that with our usual chemical methods we are not able to distinguish these different proteids, only some groups are distinguishable. Other methods are therefore used but their value is not generally acknowledged. I mean, of course, the methods of serology. By means of these whole genealogical systems have been constructed, based on the supposed chemical properties and affinities of these proteids, but critics of these methods have practically exploded them. Only a few principles of serology can be mentioned here; to enter into detail would lead us too far.

The main principle is, that definite products brought into the blood circulation of any mammal, e. g. a rabbit, cause these organisms to produce compounds which are able to check the damage caused by injection of the solution.

The injected compound is called an antigen and the whole serum-diagnosis is founded on the principle, that these antigens have a specific action. In constructing a genealogical tree with the aid of these antigens it is assumed that:

1°. each species produces compounds which are able to act as antigens;
2°. the more these antigens differ, the further removed from each other in the genealogical system are the species which produce them.

In the opinion of Mez (8) these antigens are proteids of the nucleus, especially from the chromosomes, a supposition which might account for their specific pecularities and properties. The supposition may be correct but the methods by which the antigens are extracted from plant tissues do not furnish the least proof of the hypothesis that the chromosome-proteids are present in the above mentioned solutions.

If a solution of such an antigen is injected into a rabbit an antibody is formed in the blood, which immunises the animal. This antibody can be isolated and gives a precipitate with the antigen. It is, however, questionable, whether the last-named reaction may be called speciifc; in other words, does a solution of the antibody under the required circumstances give a precipitate with the antigen obtained from this one species (and eventually the species closely allied with it), whilst no precipitate is obtained with the antigen from other species? Suppose that the latter is really the case; then the question arises: is it possible to judge the degree of affinity by the degree of intensity of the reaction? It is evident that a multitude of questions arises, which renders the diagnostic value of the whole of serology highly problematic.

With a high degree of probability it may, however, be maintained that each species has its own specific chemical compounds; for many genera the same holds good. It is also obvious for a number of families e. g. *Cruciferae, Papaveraceae, Umbelliferae, Labiatae,* etc.; whether it is true for all families has still to be ascertained.

In this connection I wish to say something about the work of the American botanist McNair (6). The latter has studied families with alkaloids, glycerides or volatile oils in reference to:

1°. the average molecular weight of the alkaloids;
2°. the average iodine value (indicator of the number of double bonds) of the glycerides);
3°. the average specific weight of the volatile oils.

McNair represents the evolutionary degree of the family by the index number which De Dalla Torre and Harms (2) have given to the families. By doing this McNair arrives at the following conclusions.

If we pay attention to families with species of the same climatic zone, the average chemical and physical properties of these families vary with the degree of evolution according to the classification of Engler and Gilg.

Putting it more precisely we can say: McNair maintains that the degree of evolution of a plantfamily is the higher:

1°. as the alkaloids possess a higher average molecular weight;
2°. the higher is the average iodine value of the glycerides;
3°. the larger is the specific weight or the lower the refractory index of the volatile oils.

Against this reasoning of McNair very serious objections may be brought forward:

1°. a pedigree can never be represented by a single line; the index numbers of De Dalla Torre and Harms are therefore wholly unfit indicators of the degree of evolution, even if we suppose that the classification of Engler and Gilg gives a fair representation of the development;

2°. whether glycerides with a higher iodine value are more complicated than those with only single bonds, is very doubtful; it is possible that on the contrary the glycerides with only single bonds are formed in metabolism from those with double bonds;

3°. the molecular weight of alkaloids depends on the ubiquitous product of metabolism from which they have originated, e. g. an alkaloid which can be derived from tryptophane (molecular weight 204) has, of course, a higher molecular weight than a derivative of proline (molecular weight 105), even if the latter is derived in a more complicated manner.

Although the work of McNair may claim the merit of drawing attention to the fact that the more closely plants are related, the more similar are their chemical products, his further considerations are to my thinking not of much value.

This, however, does not alter the fact, that a close relation exists between the nature of the chemical products and the taxonomical position of the species, genus or family which produce them. It is my intention to put the question whether each family has its own characteristic combination of chemical compounds produced in their metabolism, to the test; perhaps a better insight into the chemism of metabolism may thereby be obtained.

Literature.

1. BAKER, R. T. and SMITH, H. G., Researches on the Eucalypts, especially in regard to their essential Oils — Sidney 1902.
2. DE DALLA TORRE & HARMS, Genera Siphonogamarum ad Systema Englerianum conscripta — Leipzig 1907.
3. IVANOW, SERGIUS, Die Evolution des Stoffes in der Pflanzenwelt und das Grundgesetz der Biochemie — Ber. d. D. bot. Ges. 44, 1926.
4. JACOBS, W. J., Biol. Chem. 108, 1935.
5. LEHMANN, C., Studien über den Bau und die Entwicklungsgeschichte der Oelzellen — Planta I, 1926.
6. MCNAIR, J. B., The evolutionary Status of Plant Families in Relation to some chemical Properties — Am. Journ. of Bot. 23, 1934.
7. ——, Angiosperm Phylogeny on a chemical Basis — Bull. Torrey Bot. Club 62, 1935.
8. MEZ, C., Die Bedeutung der Serodiagnostik für die stammesgeschichtliche Forschung — Bot. Archiv 16, 1926.
9. PICTET & ROTSCHY, Compt. Rend. Ac. Sc. 132, 1901.
10. ROCHLEDER, F., Beiträge zur Phytochemie, 1847.
11. SCOTT MONCRIEFF, ROSE, Biochemical Survey of some Mendelian Factors for Flower Colour — Journal of Genetics 32, 1936.
12. SPÄTH, E., Ber. d. D. chem. Ges. 68, 1935.
13. TSCHESCHE, Die Konstitution der pflanzlichen Herzgifte — Zeitschr. f. angew. Chemie, 1934.
14. WARBURG, CHRISTIAN, GRIESEN, Biochemische Zeitschrift, 1935.
15. WEEVERS, TH., Die Bildung aromatischer Stoffe und Terpene in der Pflanze — Proc. Kon. Akad. van Wet. Amsterdam 37, 1934.
16. ——, A Consideration of some phytochemical Problems — Proc. Kon. Akad. van Wet. Amsterdam 39, 1936.