[FROM THE OFFICE OF DRUG PLANT, POISONOUS PLANT, PHYSIOLOGICAL AND FERMENTATION INVESTIGATIONS, BUREAU OF PLANT INDUSTRY, DEPARTMENT OF AGRICULTURE.]

THE RELATION OF THE ODOROUS CONSTITUENTS OF CERTAIN PLANTS TO PLANT METABOLISM.[1]

BY FRANK RABAK.

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Nature of Plant Odors.—In the vegetable kingdom there occur large numbers of plants possessing peculiar aromatic odors, by means of which the plant may ofttimes be characterized. The substances which impart these peculiar odors to plants do not consist of single compounds but mixtures of a number of compounds in varying proportions. In no instance may the aroma of a plant be ascribed to any one substance. Frequently, however, one constituent is observed to predominate over all others, its odor seemingly standing out by itself from the complex mixture. Usually this constituent attracts attention as the odor bearer of the plant.

Plant odors, owing to their volatility with steam, may be separated from the plants by steam distillation, an essential oil resulting, which bears the natural odor of the plant in a concentrated form. These oils are mixtures of numerous aromatic substances which possess definite chemical composition. The compounds which supply the aroma to plants or to the essential oils may be resolved by classification into several groups of organic compounds, namely, hydrocarbons, acids, alcohols, esters, aldehydes, ketones, oxides, phenols, lactones, and sulfur compounds.

Although all of the groups mentioned contribute to the complex odor of the plants or the volatile oils, usually there exist in the oils compounds which seem to attract one as being especially agreeable and fragrant to the sense of smell. The bearers of these pleasant odors, which are so apparent, even in complex mixtures, may generally be stated as being either ester-like or alcoholic in character.

Esters and Alcohols.—The esters represent a class of constituents which are formed by the interaction of alcohols and acids (esterification), there resulting, by the elimination of water, an *ester*. Almost invariably these esters possess a pleasant odor and convey the characteristic mellowness and fragrance to many of the essential oils. Indeed, a number of volatile oils are valued solely according to the percentage of esters which they contain.

The largest number of pleasant smelling esters are usually found in the oils as formates, acetates or butyrates, the acetic acid esters prevailing.

[1] Read at the Minneapolis meeting of the American Chemical Society. Published by permission of the Secretary of Agriculture.

The oil of lavender flowers, for instance, owes its agreeable odor to the acetic acid ester of the alcohol linaloöl or to the *linalyl acetate*. The oil is valued according ot the percentage of linalyl acetate which it contains, although the free alcohol, *linaloöl*, also exists in the oil.

In this connection may also be mentioned the methyl ester of anthranilic acid, which imparts the characteristic orange odor to oil of orange flowers. Although present in the oil to only a small extent, the orange odor is entirely due to this ester. This constituent is also present in the very fragrant ylang ylang oil, together with several other esters, among them benzyl acetate and the methyl ester of benzoic acid.

Furthermore, it may be stated peppermint oil, although consisting chiefly of the alcohol menthol, nevertheless owes its agreeable fragrance not to the menthol but to the acetic acid ester of menthol, the *menthyl acetate*. An oil rich in menthyl acetate may readily be detected by means of the smell, so characteristic is the odor of this ester.

Effect of Climatic Conditions upon Certain Plant Odors.—The exact role which plant metabolism plays in the formation and production of esters in the plant is at present not clearly understood. It may be stated with some assurance that during the growth and development of the plant changes are taking place in the form of reactions, an upbuilding of the aromatic constituents gradually resulting. Several conditions may serve to accentuate these reactions within the plant organs, as the effect of the season, the amount of sunshine and cloudiness, heat and cold, and excessive dryness or humidity.

Inasmuch as the odorous constituents of some plant are not constant in quantity in an oil, varying somewhat from one season to another, it seems that the climatic conditions mentioned above may in a measure be responsible for this variability. It is very evident that these conditions exert some effect upon the growth of the plant, either retarding or accelerating it, and consequently assisting in the formation or destruction in the plant of the aromatic constituents.

In order to illustrate more clearly the effect of seasonal changes upon volatile plant constituents, a practical observation will be mentioned.

During August, 1904, there was distilled in South Dakota a quantity of the composit plant, *Erigeron canadensis* or Canada Fleabane, a yield of 0.66 per cent. of volatil oil resulting. The same plant distilled at the same time during 1905 yielded but 0.52 per cent. of oil, while a distillation during August, 1908, produced 1 per cent. of essential oil.

The effect of the seasons or conditions of climate upon the percentage yield of oil is rather striking. The plants in the experiment were distilled in the fresh state, all conditions of distillation being identical.

To further illustrate the effect of climatic changes upon the oil, it may be mentioned in connection with the above experiments, that the quality of the oils was equally as variable as the quantity.

The percentage of esters and free alcohols (the odorous constituents) in the oils varied as follows:

Oil of Erigeron distilled in 1904, 37.8 per cent. of esters,[1] free alcohols,[1] none.
Oil of Erigeron distilled in 1905, 13.6 per cent. of esters, free alcohols, 8.7 per cent.
Oil of Erigeron distilled in 1908, 22.4 per cent. of esters, free alcohols, none.

The varying quantity of esters in the three oils is remarkably striking, especially in the 1904 and 1905 oils. The presence of 6 per cent. of free alcohol in one oil also suggests the probable effect of the climatic conditions exerted upon the plant during that season.

Another plant which also bears out this point clearly is the *Mentha citrata* or bergamot mint.

The fresh plant distilled September 10, 1907, in full blossom produced 0.37 per cent. of essential oil which by assay indicated 33 per cent. of esters, calculated as acetates of the alcohol linaloöl, $C_{10}H_{18}O$. The same plant, distilled under like conditions September 20, 1908, yielded the same per cent. of oil, but the amount of esters calculated as linalyl acetate was increased to 55 per cent.

It becomes self-evident, therefore, that changes of climatic conditions during the growth of the plants serve as important factors in the production of an essential oil during the life processes of the plant, and assist to bring about chemical changes which have a tendency to alter the constituents in a material way.

Effect of Drying upon Certain Odorous Constituents.—In order to further emphasize the fact that certain plants may undergo noticeable changes with regard to their volatil constituents during growth by responding to changes due to variation in climate, the effect of cutting and drying of a plant was studied.

Equally characteristic variations were observed in the oils distilled from plants cut and dried in sunlight.

In this experiment, the Erigeron herb was used. Parallel to the distillation of the fresh plant in August, 1904, which produced an oil containing 35 per cent. of esters and which disclosed an absence of free alcohols, a quantity of the herb from the same field was collected and dried and then subjected to distillation. The percentage of oil obtained was much less than from the fresh herb. The oil when assayed proved to contain but 18.2 per cent. of esters or approximately only one-half the amount observed in the fresh herb oil. On the other hand, this oil possessed 10.98 per cent. of free alcohol while the fresh herb oil was entirely devoid of alcoholic constituents.

The results observed seem to indicate that possibly during the drying process by the assistance of the enzymes and oxidases contained in the

[1] The esters were calculated as acetates of the alcohol $C_{10}H_{18}O$ and the free alcohols as $C_{10}H_{18}O$.

plant together with favorable conditions of heat and light, there was effected a partial decomposition of the esters with the formation of alcohols.

Effect of Flowering upon Certain Odorous Constituents.—For the determination of the effect of the flowering of a plant upon the odoriferous components, a series of experiments was carried out. The experiments consisted in the distillation of the fresh plant at three stages of its growth, namely: (1) *Before flowering* or while in budded state, (2) *at flowering*, and (3) *after blossoming* or during fruiting stage.

Only the effect of the successive stages of development upon the esters and alcohols will be considered, although the other constituents and principally the terpenic compounds may also suffer changes in quantity.

The three plants selected are typical of plants in which esters and alcohols play an essential part. The following tabulations will serve to show more clearly a comparison of results, the date of each picking and distillation being given, also the percentage yields of oil in each instance, and finally the percentages of ester and free alcohols:

TABLE A.
Mentha piperita.
Peppermint.

Stage of growth.	Date.	Percentage yield of oil.	Ester content menthyl acetate. Per cent.	Alcohol content free menthol. Per cent.
	1908			
Before flowering	7/22	0.23	9.5	31
Flowering	8/21	0.20	14.5	23.6
After flowering	9/25	0.10	24	34

TABLE B.
Mentha citrata.
Bergamot mint.

Stage of growth.	Date.	Percentage yield of oil.	Ester content calculated as linalyl acetate. Per cent.	Alcohol content calculated as linaloöl (free). Per cent.
	1908			
Before flowering	7/20	0.32	47.6	7.3
Flowering	9/22	0.37	55	7.3
After flowering	10/14	0.22	52	5.5

TABLE C.
Artemisia absinthium.
Wormwood.

Stage of growth.	Date.	Percentage yield of oil.	Ester content thujyl acetate Per cent.	Alcohol content thujyl alcohol (free). Per cent.
	1908			
Before flowering	7/2	0.19	26	14.7
Flowering	7/14	0.18	32.5	11.7
After flowering	8/4	0.10	47.5	12

In consideration of oil of peppermint (Table A) it becomes obvious at a glance that the yield of oil remains practically unchanged during the first two stages of growth, the third stage reducing the yield about one-half. The percentage of the odorous constituent, menthyl acetate, in the oil increases successively, the oil from the "after flowering" stage being exceedingly and noticeably more fragrant than either of the other oils. The free menthol content, however, does not exhibit the steady increase, varying from 31 per cent. in the oil of stage 1, to 23.6 per cent. in the second, and 34 per cent. in the third oil.

The blossoming of the plant seems to have no effect upon the consumption of esters while a slight diminution of free menthol is observed. This, however, was not permanent as the oil distilled a month later again shows an increase in free menthol as well as menthyl acetate.

Whether the peppermint plant, during the course of its growth from the budding period to the fruiting stage, consumes any of the above-mentioned substances is doubtful. It may be concluded, nevertheless, that the plant after passing into the last stage of development does consume other constituents of the oil, thus leaving an oil richer in both esters and alcohols.

In Table B, the yields of oil from the plant *Mentha citrata* follow a similar course to those of the preceding plant, the first and second stages of growth were nearly identical in yield of oil with a sharp diminution in the third stage (after flowering). The content of ester calculated as linalyl acetate reaches its maximum in the oil distilled from the flowering plant, although the percentage of ester in the oil from the plant after flowering was only slightly decreased. The content of free alcohol in the oils remains the same in oils I and II, whereas oil III discloses a slight lowering.

It would seem from a careful consideration of these facts that the plant *Mentha citrata*, which owes its lavender-like fragrance to the esters present, produces at its flowering stage the maximum quantity of ester, which apparently diminishes but little, even after the plant has entered its fruiting condition. As in the case of the peppermint there may be a slight destruction or consumption of some of the terpenic compounds in the oil during the metabolic processes in the third stage of growth, the esters and alcohol remaining practically unaltered.

In the case of the wormwood plant (Table C) much the same conditions exist. The yields of oils follow the same course as the other plants with a sudden drop in the "after flowering" stage.

The percentage of ester, thujyl acetate, reveals a steady increase from 26–32.5 per cent. to 47 per cent. in the three stages of growth. Again there appears to be little if any consumption of the odoriferous compounds by the plant during its advancement, either of the esters or of the thujyl alcohol.

Conclusions.

In general, it may be asserted with some degree of assurance that the odorous constituents, the esters, of the aforementioned oils do not manifestly seem to be affected during fructification of the plant. However, in all cases there does appear to have been a period during the growth and development of the plants when, with the assistance of certain favorable conditions, the chemical processes in the plant transformed some of the basal constituents into esters and corresponding alcohols.

The steady upbuilding of the ester compounds in the plants as the advancement of the plants proceeded is strikingly apparent. The percentages of free alcohols seemingly bear but slight relationship to their corresponding esters or to the life processes of the plant.

That the odorous constituents formed in plants are simply products of excretion formed during the metabolism of the plant, and are of no further use to the plant, seems probable, since the plants do not obviously utilize these stored-up compounds for any special purpose other than a possible means of protection against insect enemies from which most aromatic plants are notably free.

It has been shown how the processes of metabolism in the plants were influenced under varying conditions of climate (different seasons); also the effect of drying, and lastly the effects of budding, blossoming, and fruiting upon the life processes of the plants, resulting in every instance in changes in the aromatic constituents, but in no instance was a decided consumption of the ester or alcoholic constituents observed.

WASHINGTON, D. C.

NEW BOOKS.

Contribution a l'Histoire de la Chimie a Propos du Livre de M. Ladenburg sur l'Histoire du Developpement de la Chimie depuis Lavoisier. Par A. COLSON, Professeur a l'École Polytechnique. Paris: A Herrman et Fils. 1910. pp. 130. Price, 3 francs.

Professor Colson, after expressing his admiration for the historical work of Ladenburg, mentions certain conditions in France which hinder any foreigner from accurately estimating the science of France. He therefore treats of some points in the history of chemistry which in France are thought of more highly than seems to be the case in Germany. The tone of the little book is excellent; read in connection with Ladenburg, to which references are numerous, it will give a helpful and interesting view of the brilliant contributions to chemistry which have been made by the countrymen of Lavoisier. EDWARD W. MORLEY.