LXXXIII. ESSENTIAL OILS AND HEAT ABSORPTION.

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EFFICIENS est calor Solis qualitatem educens et extrahens. (Themata physica de odorum natura et affectionibus.) [Iohannes Camerarius: Marburg; 1587. Quoted by Kenneth, 1928]. Tyndall [1875 and earlier] was the first to establish that water vapour in very small amount appreciably absorbed heat in the form of radiant energy. His finding was confirmed spectroscopically by a large number of workers and is now a scientific commonplace. Tyndall also investigated the heat absorption of essential oil vapours, but, although his work is mentioned by many botanists and writers on perfumes, only one later worker appears to have investigated this question experimentally. Grijns [1919], who used a modification of Tyndall's apparatus, included only three essential oils in his series; but he found absorption of heat by volatile substances to be much smaller than the degree claimed by Tyndall.

A quantitative estimate of heat absorption by vapour is of possible importance to the evaluation of essential oils, and in problems of the physiology of odour, and of the rôle of the essential oil in the plant. An attempt was made to investigate the heat absorption of odoriferous substances. Two methods were used. The first was based upon the conversion of intermittent energy into sound [Tyndall, 1880, 1]. It was hoped that this method might be made sensitive by the use of thermionic amplification, but it was not possible to find reliable conditions or to obtain sufficiently intense sounds. Tyndall [1881, 2] made some remarkable claims as to the intensity and variation of sound obtainable but the experimental details he gave are meagre. It is perhaps noteworthy that Rayleigh [1903], in discussing this part of Tyndall's work, made no reference to any intensity of sound greater than that obtained by the present author. This part of the work was abandoned in favour of the thermopile method.

Preliminary experiments with vapours in a long glass tube through which radiant heat was sent to impinge on the face of a thermopile in air, failed to show any appreciable absorption due to the vapour of essential oils. At an early stage the difficulty of obtaining sufficiently large plates of rock-salt became evident. Several suggested substitutes were tried and found to be nearly opaque to radiant heat originating at the temperature of boiling water.

A special journey to the region of Salzburg, in Austria, and to Stassfurt, in Germany, was made [Nicol, 1928] and a supply of salt obtained. Much time was spent in acquiring the technique of working suitable pieces into plates.

Preliminary experiments, in which the vapour was enclosed between rock-salt plates in a glass tube, were considered inconclusive owing to the double passage of the heat rays through air at entry into and exit from the tube. Tyndall took elaborate precautions to pass his entering rays through a vacuum only, but he placed the receiving thermopile in air. Although Tyndall's thermopile was "compensated," it appeared desirable to make the apparatus self-contained. The final form, which was intended to be tentative only, was as follows.

A vertical brass tube 5.3 cm. internal diameter and 53 cm. long was closed at the upper end by a brass chamber through which steam was passed. The common wall of this chamber thus supplied the source of heat at approximately 100°. At the lower end was a removable circular diaphragm supporting a thin plate of rock-salt. Beneath this was a chamber forming a prolongation of the tube, and containing a thermopile cube insulated from the bottom of the tube. The lower end of the brass tube was immersed in a bath in solid paraffin wax to keep the temperature of the thermopile chamber approximately constant. Leads to a galvanometer were provided. An inlet tube for vapour was provided just below the steam-chest. In series with this inlet was a wider glass tube into which a porcelain boat or other container for essential oil could be inserted; during part of the experiment this tube was fitted with leads to a gold-leaf electroscope from wires dipping into the oil. Before passing over the oil-boat, air was freed from carbon dioxide and moisture by means of an apparatus consisting of 10 tubes each a metre long filled, in order, respectively: 2 with 40 % caustic soda solution, 2 with soda lime, 2 with concentrated sulphuric acid, 1 with "20 %" fuming sulphuric acid and 3 with sulphuric acid. An outlet was provided just above the diaphragm supporting the salt plate, and an exhaust tube was also provided for the thermopile chamber. The two latter tubes were connected, and stopcocks were fitted so that either or both chambers could be put into communication with each other or with a vacuum pump.

The apparatus in principle resembled that of Magnus [1861] more than Tyndall's and was open to the objection that it was impossible with it to eliminate entirely the effects of convected as distinct from radiant heat. It was also crude in that it failed to exclude heat conducted along or radiated from the walls of the tube, and that the thermopile was not compensated. It would now be possible to design a more satisfactory apparatus, although this would be extremely costly.

The design of the apparatus was not, however, of importance. Work performed with it suggested—as will be shown—that frothing of the oil indicated the presence of water in practically all of the substances tested, and this phenomenon of frothing took place outside, and was independent of, the thermostat chamber. On account of this simple demonstration of a factor of which the importance had been underestimated by Tyndall and ignored by later commentators, it became superfluous to refine the design of the apparatus, inasmuch as it was intended to detect the absorption of radiant heat by commercial samples of essential oils.

As a preliminary *experimentum crucis*, many attempts were made to determine whether the heat absorption from a source at approximately 100° of dry air was negligible, as found by Tyndall. When the rock-salt plate was not in position, and the air was allowed to come into contact with the thermopile

(the galvanometer reading having become steady with the tube exhausted or nearly so) a reading was in all cases obtained, which indicated heat absorption. Only very little less absorption was indicated when dry air was used than when room air was used. The reading with dry carbon dioxide was similar to that with dry air. With dry hydrogen, an enormous "absorption" was indicated in similar circumstances, but the absence of any indication of heat absorption by hydrogen when that gas was prevented by the salt plate from surrounding the thermopile cube, suggested that the apparent absorption was due to the combined cooling effects of conduction and convection upon the thermopile itself¹. It was therefore decided to leave the question of the absorption by water vapour and investigate the problem of the absorption by volatile essential oils.

The first experiments with oils were, as before, made while allowing air to come into contact with the thermopile, before entering the exhausted tube, but the air was passed over the essential oil. Alternatively, the chamber containing the vessel of essential oil was exhausted either simultaneously with the tube, or by putting the oil chamber into communication with the tube after the latter had been exhausted. The last mentioned process was sometimes repeated in order to reach a sufficient degree of exhaustion in the apparatus. It was thus hoped to obtain indications of absorption (a) of the oil vapour in presence of varying pressures of air, and (b) of the oil vapour in equilibrium with oil, which was in all cases at room temperature.

In the course of these experiments, however performed, it was noticed that the oil appeared to froth or "boil" when the pressure became sufficiently low. Moreover, this phenomenon having occurred once with a given sample of oil, could not usually be repeated with the same sample of oil, however high the vacuum might be or however long it might be maintained. If the pressure were reduced in stages as mentioned above, it sometimes happened that a small degree of frothing was followed by one more intense at a lower pressure, after which the frothing could no longer be induced even with a high degree of vacuum. Simultaneously with the frothing, a deflection of the galvanometer was noticed, indicating apparent absorption of heat, but when the frothing had ceased the galvanometer reading returned to its former level. These findings were repeatedly confirmed with various oils. In one case (after the frothing) several cc. of geranium oil distilled over at room temperature and condensed beyond the experimental tube, in the tubing leading to the pump, without any deflection of the galvanometer being seen during the passage of so much supposedly heat-absorbing material through the tube.

It was concluded that the frothing, and the absorption of the heat which accompanied it, were due to the evaporation of water from the oil. Chemical consideration of the comparative water-solubilities of the constituent oils gave support to this hypothesis. A qualitative study was made of the electrical

¹ The well-known experiment of the glowing wire successively *in vacuo* and surrounded by hydrogen offers an analogy.

conductivity of the essential oil used, with a view to seeing whether any relation existed between the conductivity and the amount of frothing exhibited by the oils under the conditions described. For this purpose the device mentioned above was used, but the gold-leaf electroscope was found to be too sensitive an indicator; its reading was nearly as large in most cases after the frothing of oils as with the original oil. A modified method was devised of determining the order of conductivity and an account of results obtained with it has been published [Nicol, 1929]. It was found that the intensity of frothing of the oils, and their ability to conduct electricity, were very closely related.

With the salt plate in the tube, further experiments were made upon essential oils, and the frothing effect was disregarded. It was found that a steady current of dry air passed over oil from which the water had been almost completely boiled off (as determined by the cessation of frothing) had an almost insignificant heat absorption, hardly exceeding the experimental error. The magnitude of the effect varied and it was apparently zero with some oils.

Pure esters and other organic compounds were examined in addition to essential oils. The four benzoates tried showed diminishing water content with increasing molecular weight. The following is a list of substances examined, named in the order of increasing degree of frothing under diminished pressure. In some cases samples from two sources were tested. The order closely follows the order of the electrical conductivities, and turbidities on addition of turpentine [Nicol, 1929]. The groups are necessarily not sharply distinguished.

I. Hydrophobe group.

(a) Turpentine.

(b) Benzyl benzoate: *iso*amyl benzoate: safrol; oils of rosemary, white thyme¹, red thyme, aniseed (badiane), bergamot, limes distilled, eucalyptus (globulus), lemon, sweet (Portugal) and bitter orange, limes expressed², lavender (French), cananga, mandarine (tangerine), ylang-ylang, cajuput, citronella (Ceylon), patchouli.

II. Hydrophile group.

Oils of citronella (Java), petitgrain, cinnamon bark; ethyl benzoate, methyl salicylate, methyl benzoate; oils of palmarosa, cloves (English distilled), geranium (African), cinnamon leaf, lemon-grass; anisaldehyde; oil of cassia.

DISCUSSION.

No worker familiar with Tyndall's researches on the absorption of heat by water vapour could avoid being impressed by the extreme care which was taken by Tyndall in most of his work to remove minute traces of water vapour from the dried gases which he used. With the chemistry of the essential oils,

¹ Redistilled oil of red thyme.

² And subsequently distilled.

Tyndall appears to have had no especial acquaintance. He was aware that they might contain small amounts of water, and it is noteworthy that in his experiments on the absorption of heat by essential oil vapours, Tyndall practically neglected the possibility of an effect due to water vapour. He remarked that the amount of water vapour could only be "infinitesimal." It is also striking that perfumery workers who have subsequently commented on this work, have, presumably through ignorance of Tyndall's complementary investigations, failed to realise the importance of the water content of most essential oils. The amounts of water present in commercial oils are, in general, quite appreciable. The present author, like others conversant with the chemistry of essential oils, also overlooked the possibility of interference from water vapour until the point was brought home to him by the "frothing" mentioned above, for which no explanation suggested itself immediately.

The initial conductivity of the oils ran apparently *pari passu* with the intensity of the "frothing" they exhibited under reduced pressure. No figures are available in support of this point, since the "frothing" was not susceptible of measurement.

It was found that the least frothing and the least conductivity were possessed by turpentine, safrol, benzyl benzoate, and the oils of the citrus fruits. The greatest frothing and the maximum of conductivity were shown by lemon-grass oil, cinnamon leaf oil, cassia oil and anisaldehyde. It appeared, generally speaking, that the water contents of the oils varied inversely with their terpene contents and directly with their phenol and aldehyde contents. A confirmation of the two foregoing methods of ranging the oils in their order of water content was afforded by the qualitative examination of the turbidity produced when each was added to turpentine.

The botanical significance of these results is quite different from that which it was sought to determine. It was originally desired, *inter alia*, to test the hypothesis that some essential oils acted as a heat screen for the plant which elaborated them. This hypothesis could not be of general application to all oils, since there are some, such as camphor, which normally do not come into contact with the surrounding air, and others, such as the citrus oils which are elaborated in proximity to the exterior walls of a part of the plant yet do not appear to volatilise appreciably from it.

Dixon [1914] wrote: "It is a matter of frequent observation that many plants which are natives of arid regions secrete a relatively large amount of ethereal oils. It has been urged that the vapours of these ethereal oils form a screen which arrests the heat radiations, and thus the leaves of the plant are kept cooler than otherwise would be....Such an absorptive screen in contact with the leaves...would rather tend to raise their temperature." He suggested that the action of essential oil vapour in checking evaporation and transpiration would afford a simpler explanation of the function of the oily secretions. In a simple experiment he found that vapour given off from chopped leaves of *Artemisia absinthium* considerably reduced the rate of

transpiration of a branch of *Syringa vulgaris*. Dixon's researches might possibly be extended with advantage.

The outstanding botanical outcome of the present results is the distinction, by a method independent of any hypothesis concerning the structure or habit of the plant, of oils borne by plants of xerophyte type (conifer, labiate (rosemary and thyme) and citrus fruits), and those oils elaborated in continuous intimate contact with aqueous liquids. In the first class, the oil is formed during a desiccative process, and is hydrophobe; in the second class, the oils are continuously formed in and remain in contact with, the protoplasm until they are volatilised. It is possible that oils of the second class are frequently present as glucosides [*cf.* Hampton, 1925].

It would be of interest to compare, from the standpoint of water-retaining capacity, oils from flower and fruit of the same plant, as, for example, the orange, which yields orange-flower oil, petitgrain oil (from immature fruits) and orange oil from the *zeste*. Owing to the cost of the flower oil, and to the practical impossibility of obtaining a sample of indubitable origin, this point has not been tested as regards orange-flower oil, but it was found that petitgrain oil had indications of an appreciably higher water content than ordinary orange oil from peel of the mature fruit. In amplification of this finding, it may be noted that orange-flower water, like rose water (which contains notable amounts of the water-soluble alcohols) is an article of commerce, whereas the water separated from orange oils is of no commercial value and contains only traces of odoriferous substances.

With regard to the heat-screening hypothesis, it is evident that this hypothesis can apply if at all, only to some of the odoriferous oils secreted by plants. Whether it applies to any of them appears doubtful, and the author shares the view of Dixon concerning the physical dubiety of the hypothesis. Schübeler [1880] found in "vegetation developed under the influence of short summers with almost continuous light" "that the aroma of fruits is increased and that the development of essential oils in certain plants is greater than in the same plants grown in other latitudes."

Freund [1904] quotes a statement that the effect of coloured light on growing plants "is greatest on the scent. Thus, strawberries grown under red glass have a wonderful aroma, and crassula flowers, which are nearly scentless in ordinary sunlight, emitted a delicious fragrance, like that of bananas, under the influence of red light."

Commercial essential oils are usually steam-distilled, and contain water derived from the distillation. It was such oils, not further dried, which were used by Tyndall, and by the author in the present work. Do these commercial oils contain water in amount different from that which they contain in the plant? What are the phases of the oil and the water?

In view of the difficulty that exists in determining the absolute water content of commercial oils, the first question appears likely to remain open. The second question is of greater interest. In the estimation of relative water

content by a conductivity method it was assumed that the ordinary oil is either (a) a suspension of oil in water or a true solution: it may be, a solution of oil in an aqueous solution of water-soluble constituents¹, or (b) a suspension of water in oil. If the oil is a suspension of water in oil, a large amount of water might be present without a significant conductivity being detected. In view of the concordance of the conductivity determinations with the relative turbidities, it appears probable that most essential oils contain oil either in aqueous suspension or in water. The behaviour of turpentine is singular, and it is therefore suggested that, in so far as a turpentine-water mixture tends to form a suspension, water is suspended in the turpentine. Parry [1925] makes a sharp distinction between conifers, in which the oil ducts are lysogenic, and the Rutaceae and many other plants in which the ducts are schizolyso-genic or of mixed origin.

SUMMARY.

The classical work on absorption of radiant heat by the vapour of essential oils is in error owing to neglect of the water content of the latter. The effect is chiefly due to water vapour and only secondarily to the odoriferous constituents.

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¹ This may not appear clear at first reading so an analogy is offered. If clove oil, containing substances soluble and insoluble in aqueous sodium hydroxide solution, is shaken with that solution the apparent solubility is frequently greater than the true solubility. This is due to substances dissolving in the resulting phenolate solution which were not soluble in sodium hydroxide before the phenols were taken up by the soda. In the oils referred to in the text, a water solution of part of the oil (*e.g.* of the lower alcohols) may dissolve more of the remaining oil than would pure water.

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