VIII. Examination of select Vegetable Products from India.

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PART I.

THROUGH the kindness of my esteemed friend Dr. Royle, I have been permitted to select such vegetable products from the extensive collection at the India House as seemed most likely to repay the trouble of investigation. My attention during the last twelve months has been chiefly directed to three of these vegetable substances; and the results of their examination I now take the liberty of submitting to the Royal Society, to be followed by those of the others as they may be completed.

Datisca cannabina.

The first of these substances which I examined consisted of a quantity of the roots of the Datisca cannabina, from Lahore, where this plant is employed to dye silk of a fast yellow colour. The roots, which had been cut into pieces about six or eight inches long, were from one-half to three-quarters of an inch in thickness. They had a deep yellow colour. The leaves and smaller branches of the Datisca cannabina from the Levant have long been employed for a similar purpose in the South of France. A decoction of the leaves of the Datisca cannabina was examined by Braconnot in 1816, who discovered in it a crystallizable principle to which he gave the name of datiscine. Braconnot, of course, did not subject this substance to analysis, but he described its appearance and properties in an exceedingly accurate manner*. observations of Braconnor had fallen into such entire oblivion, however, that for many years past, we find in most of the larger systems of chemistry the term datis-Thus in Brande's 'Chemistry,' vol. ii. cine used as synonymous with inuline. page 1168, we find it stated that a variety of names had been given to inuline, such as "dahline, datiscine," &c. In Löwig's 'Chemistry of Organic Compounds,' vol. i. page 359, the same error is repeated, where, under the article "inuline," the synonyms given are "dahline and datiscine."

The bruised roots were extracted in a Mohr's apparatus by long-continued digestion with wood-spirit. The liquor obtained, which had a dark brown colour, was concentrated by distilling off a portion of the wood-spirit. The brown syrupy liquid remaining in the retort, on being poured into open vessels and standing for some

* Annales de Chimie et de Physique (1830), iii. 277.

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time, deposited a resinous matter containing merely traces of a crystalline substance. When this syrupy liquid, however, was treated with about half its bulk of hot water, the greater portion of the brown resin was rapidly deposited, and the mother-liquor, having been poured off and left to slow spontaneous evaporation, deposited a considerable quantity of an imperfectly crystallizable substance resembling grape-sugar. These crystals are impure datiscine, still retaining a considerable amount of resinous matter, to which the dark brown colour is owing.

They may be purified in various ways, advantage being taken of the greater solubility of the resinous matter in alcohol or ether, than that of the datiscine. By repeated crystallizations, therefore, from either of these liquids, the datiscine may be rendered almost perfectly colourless, the impurities remaining in the mother-liquor. The following is the method which I have found, on the whole, most convenient. The crude datiscine, while still moist, is strongly pressed between folds of blotting-paper; it is then dissolved in alcohol, and again treated with water, which throws down the resin. The diluted alcoholic solution, after standing some time, yields the datiscine in a much finer state. On repeating this operation several times, the datiscine may be obtained perfectly pure. In order to separate any traces of tannic acid which might have been present, I repeatedly added a concentrated solution of gelatine to the alcoholic solution of the datiscine, and after careful filtration, precipitated the datiscine in the way already described. I could not, however, observe that the crystals of the datiscine, when gelatine had been employed in its preparation, were in the least degree dissimilar from the datiscine obtained in the usual way.

Properties of Datiscine.—Datiscine, when quite pure, is perfectly colourless, but unless great attention is paid to its purification, it usually has more or less of a yellow colour, varying from pale to deep yellow, according to circumstances. It is very soluble in alcohol, even in the cold, boiling alcohol dissolving almost any amount of it.

By slow spontaneous evaporation, its alcoholic solutions yield small silky needles arranged in groups. Cold water does not dissolve much of it, but it is tolerably soluble in boiling water, the hot solutions on cooling depositing it in shining scales. Ether does not dissolve much datiscine, but an ethereal solution, when allowed to evaporate as slowly as possible, yielded it in larger crystals than I could have obtained in any other way. When water is added to an alcoholic solution of datiscine, no precipitate is immediately formed, unless the solution is greatly concentrated; but on standing for some time, the datiscine separates in a very pure state, consisting of fine crystals having a pale yellow colour. The datiscine prepared by this process was found to contain but a minute trace of ash. When datiscine is heated to about 180° C., it melts, and if the heat is still further increased, it burns, evolving an odour of caramel, and leaves a voluminous charcoal. If datiscine be heated in a close vessel while a stream of dry air is slowly passed over it, a small quantity of a crystal-line substance sublimes. Datiscine and its solutions have a very bitter taste; and

though it does not produce any change upon test paper, I think there is reason to regard it as a feebly acid body. It dissolves in solutions of the fixed alkalies and ammonia, as well as in lime and baryta water. Their solutions have a deep yellow colour, which they lose on the addition of an acid, when the datiscine is precipitated, even acetic acid precipitating datiscine. When its alkaline solutions are not too concentrated, and are neutralized while hot, the datiscine on cooling is deposited in small crystals. The aqueous solution of datiscine is precipitated by neutral and basic acetates of lead, or chloride of tin. These precipitates have a bright yellow colour.

Salts of copper produce greenish precipitates; those of peroxide of iron deep brownish-green precipitates. The datiscine employed in these experiments had been purified with gelatine.

The lead salts form such gelatinous precipitates, that they could not be washed, and therefore I was unable to employ them in determining the equivalents of datiscine.

Action of dilute Sulphuric Acid on Datiscine.

When an aqueous solution of datiscine is treated with a small quantity of sulphuric acid, the clear liquid, after being boiled for a few minutes, becomes turbid, and deposits a crystalline substance. This is collected on a filter, and the clear liquid which passes through, after it has been made strongly alkaline by the addition of potash, and after being heated to 212°, throws down suboxide of copper. When the excess of sulphuric acid is removed from another portion of the solution, by neutralizing with carbonate of lead or baryta, it acquires a sweet taste; and when evaporated to the consistence of a syrup, on standing for some time, it formed a semi-crystalline mass, closely resembling honey. This experiment showed therefore that datiscine, like salicine and similar bodies, belongs to the class of glucosides, and is a copulated compound of sugar and another substance which I shall call datiscetine.

Datiscetine.—Datiscetine in its general appearance and properties closely resembles datiscine. On a closer examination, however, these two substances are found to differ essentially, both in composition and properties. Datiscine, when prepared by boiling a solution of pure datiscine with dilute sulphuric acid, precipitates in the state of fine needles, which are nearly colourless. It is easily soluble in alcohol; a hot alcoholic solution, on cooling, depositing the greater portion of it in crystalline groups. It is almost insoluble in water, and consequently datiscetine is abundantly precipitated from its alcoholic solutions by the addition of water. It dissolves in ether to almost any extent, and is deposited, on the evaporation of that liquid, in needles.

These properties of datiscetine enable us to obtain it in a tolerably pure state when even very impure datiscine is employed in its preparation. The mother-liquors out of which datiscine has been crystallized, and which retain a large amount of impurities, can be used in the following way for the preparation of datiscetine. These

liquors are first treated with basic acetate of lead, the precipitate is collected on a filter and washed, and then, having been distributed through water, is decomposed by sulphuretted hydrogen. The solution which has filtered from the precipitated sulphide of lead, is then concentrated, and boiled with dilute sulphuric acid. The datiscetine produced in this way can be easily separated from the resinous matter, as the latter is precipitated before the formation of the datiscetine by the acid, and adheres to the bottom of the flask. By dissolving the datiscetine thus obtained in alcohol, and precipitating it by the addition of water, it is rendered tolerably pure.

Properties of Datiscetine.—Datiscetine has no taste. When heated it melts like datiscine, but the heat required is much higher than is necessary for that body. It crystallizes again on cooling. By operating very cautiously, a portion of the datiscetine may be sublimed in crystals. This sublimate, however, appears to be altered datiscetine, for, when recrystallized out of ether, it has a sweet taste. Datiscetine on burning does not emit the smell of caramel.

Datiscetine, like datiscine, dissolves in alkaline solutions, and is reprecipitated by the addition of an acid. When an alcoholic solution of acetate of lead is added to one of datiscetine, also dissolved in alcohol, a finely coloured deep yellow precipitate is obtained, which can be easily washed both by alcohol and water.

This precipitate therefore was subjected to analysis.

Analysis of Datiscine and Datiscetine.—The lead salt of datiscetine, when subjected to analysis, gave the following results:-

- I. 0·4555 grm. gave 0·2060 grm. PbO. 0.2655 grm. gave 0.3515 grm. CO2 and 0.0405 grm. HO.
- II. 0.4310 grm. gave 0.1945 grm. PbO.
- III. (from another preparation).

0.4170 grm. gave 0.1907 grm. PbO.

0.3170 grm. gave 0.4195 grm. CO2 and 0.0460 grm. HO.

These analyses give the formula $C_{30} H_8 O_{10} + 2 PbO$.

| Required. | Found. | | | |
|--|---------------------------------|------------------------|-------|------------------------|
| Required. | | I. | II. | III. |
| $\begin{array}{cccccccccccccccccccccccccccccccccccc$ | 36·63 1·63 16·28 45·46 | 36·11 1·69 45·22 | 45.13 | 36·09 1·61 45·73 |

Analysis of Datiscetine.—The different preparations were all dried at 100° C. in a current of dry air, and burned in the gas furnace.

Datiscetine crystallized out of Alcohol.

- I. 0·3970 grm. gave 0·9155 grm. CO₂ and 0·1280 grm. HO.
 II. 0·4455 grm. gave 1·0275 grm. CO₂ and 0·1485 grm. HO.

Datiscine prepared from its alcoholic solution by the addition of Water.

- III. 0.2045 grm. gave 0.4715 grm. CO2 and 0.0665 grm. HO.
- IV. 0.3680 grm. gave 0.8505 grm. CO2 and 0.1245 grm. HO.

The per-centage results calculated from these analyses agree very closely with the formula deduced from the analyses of the lead salt, as shown in the following Table:—

| Required. | | Found. | | | | |
|----------------------|-------------------|---------------|---------------|---------------|---------------|--|
| | | I. | II. | III. | IV. | |
| $H_{10}^{30} = 10$ 3 | •94 •49 •57 | 62·89 3·58 | 62·90 3·70 | 62·88 3·61 | 63.03 3.76 | |

Analysis of Datiscine dried in a Liebig's drying tube.

- A. Datiscine crystallized out of alcohol.
- I. 0.3890 grm. gave 0.7815 grm. CO₂ and 0.1780 grm. HO.
- II. 0.3395 grm. gave 0.6770 grm. CO2 and 0.1585 grm. HO.
- B. Datiscine crystallized out of alcohol from another preparation.
 - I. 0.2785 grm. gave 0.5595 grm. CO2 and 0.1315 grm. HO.
 - II. 0.2905 grm. gave 0.5830 grm. CO2 and 0.1385 grm. HO.
 - C. Datiscine prepared with gelatine and out of alcohol.
 0.4145 grm. gave 0.8355 grm. CO₂ and 0.1925 grm. HO.
- D. Datiscine separated from its alcoholic solution by the addition of water.
 - I. 0.1580 grm. gave 0.3135 grm. CO₂ and 0.0770 grm. HO.
 - II. 0·1980 grm. gave 0·3955 grm. CO_2 and 0·0925 grm. HO.
- E. Datiscine precipitated from its potash solution by the addition of acetic acid. 0.2985 grm. gave 0.5940 grm. CO₂ and 0.1375 grm. HO.

The substance analysed in A. contained 0.3 to 0.4 per cent. of ash; that in B. 0.2 to 0.25 per cent.; and that in C. 0.12 per cent. No allowance, however, was made for these amounts of ash in calculating the following numbers.

The datiscine used for the analyses D. and E. did not contain any appreciable quantity of ash.

The following are the per-centage numbers calculated from the above analyses:—

| | А. | | В. | | C. | Г |). | Е. |
|-------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|---------------|
| | I. | II. | I. | II. | | I. | II. | |
| C H O | 54·79 5·08 | 54·38 5·19 | 54·79 5·25 | 54·73 5·29 | 54·97 5·16 | 54·11 5·41 | 54·48 5·19 | 54·27 5·12 |

When the decomposition of datiscine into datiscetine and sugar is taken into consideration, it seems probable that the formula for datiscine is—

Datiscetine+Sugar =Datiscine
$$C_{30} H_{10} O_{12} + C_{12} H_{12} O_{12} = C_{42} H_{22} O_{24}$$
.

That formula requires

$$C_{42}$$
=252 54.08
 H_{22} = 22 4.72
 O_{24} =192 41.20

If the formula $C_{42}H_{22}O_{24}$ be correct, the decomposition of datiscine would be analogous to salicine, which, when treated with dilute acid, gives

Salicine =Sugar +Salicetine
$$C_{26} H_{18} O_{14} = C_{12} H_{12} O_{12} + C_{14} H_{6} O_{2}$$
;

whilst when treated with emulsine,

Salicine =Sugar +Saligenine-2HO.

$$C_{26} H_{18} O_{14} = C_{12} H_{12} O_{12} + C_{14} H_{8} O_{4} -2HO.$$

The above formula for datiscine is confirmed by the following determinations of sugar formed by treating a weighed quantity of datiscine with dilute sulphuric acid. The quantity of sugar produced was estimated by Fehling's method with a standard solution of sulphate of copper. Four determinations made in this way gave the following quantities of sugar for 100 parts of dry datiscine:—

The calculation for the formula $C_{42}\,H_{22}\,O_{24}$ requires 38.6 per cent. of sugar.

An attempt was made to confirm these determinations by the direct estimation of the datiscetine formed during the decomposition of a given weight of datiscine by dilute sulphuric acid. The numbers obtained, however, during different experiments did not correspond with each other, and were all much lower than theory required. This however is not to be wondered at, as the datiscetine, though very differently soluble, is by no means absolutely insoluble in water. Dilute hydrochloric acid was found, like sulphuric acid, to decompose the datiscine into sugar and datiscetine, and even on boiling an aqueous solution of pure datiscine for some hours traces of sugar could be detected; thus showing that a small portion of the datiscine had been decomposed. It has been shown by previous experiments, and analysis No. 8, that datiscine may be dissolved in cold solutions of potash without decomposition. When boiled, however, with a concentrated potash lye for some time, decomposition takes place, and the precipitate, thrown down by the addition of an acid, has all the properties of datiscetine. In this respect, therefore, datiscine agrees with tannin and

similar glucosides, which yield the same products when acted upon by acids and alkalies; tannin from nut-galls being equally resolved by acid and alkalies into gallic acid and grape-sugar. A solution of datiscetine, when left for some time in a warm place in contact with yeast, did not ferment, and though emulsine was also tried no separation of datiscetine was observed.

Action of Nitric Acid on Datiscine and Datiscetine.

When datiscetine is treated in the cold with nitric acid of ordinary strength, a violent reaction takes place, brown vapours are disengaged, and a resinous substance produced. The heat evolved by the reaction is sufficient to continue it till all the resinous matter is dissolved and a dark red liquid produced, which after boiling becomes yellow, and when cautiously evaporated, deposits on cooling crystals of nitropicric acid. If the reaction is not carried too far no oxalic acid is formed, and the nitropicric acid obtained is very pure, forming large crystals of a pale yellow colour. The following experiments show that these crystals are really nitropicric acid.

When treated in the cold with a concentrated solution of hypochlorite of lime, the very characteristic smell of chloropicrine is instantaneously observed. The addition of a solution of potash to a second portion of the acid threw down crystals of very pure nitropicrate of potash, which, when subjected to analysis, gave 18.04 per cent. of potash, the calculated quantity required for nitropicrate of potash being 17.66 per cent. Datiscine treated in the same way yields nitropicric acid as well as oxalic acid. The formation of nitropicric acid by the action of strong nitric acid on datiscine and datiscetine, rendered it highly probable, that, by employing dilute nitric acid, less highly oxidized products of decomposition might be obtained. Datiscetine was therefore boiled with dilute nitric acid, i. e. nitric acid with ten parts of water; the crystals of datiscetine soon dissolved, and a yellow liquid was obtained, which when treated with a solution of perchloride of iron gave a blood-red colour. When the original solution had cooled, pale yellow crystals were deposited. These crystals were very soluble in hot water, and recrystallized on cooling. soluble in hot water, and recrystallized on cooling.

They were likewise very soluble in alcohol and ether, and when deposited by slow evaporation from their alcoholic solutions, they formed nearly colourless crystals of considerable size, having a fine silky lustre. When treated with hypochlorite of lime they did not evolve chloropicrine in the cold, but readily produced that compound when gently heated. When they were cautiously heated between two watch-glasses, a portion of the substance sublimed in colourless needles. When this acid was heated with an insufficient quantity of water to dissolve it, it melted and recrystallized on cooling. These properties agree with those of nitrosalicylic acid. In order to confirm this hypothesis the following salts were prepared.

On saturating a solution of the acid with carbonate of baryta, the baryta salt was obtained in vellow crystals. From their solution ammonia threw down another

obtained in yellow crystals. From their solution ammonia threw down another

yellow-coloured baryta salt. A solution of the acid likewise produced a crystallized lead salt. The ammoniacal salt was obtained in orange-coloured needles by saturating the acid with ammonia and crystallizing in vacuo. By double decomposition with the ammoniacal salt I prepared the silver combination, which, like all the others, agreed in its properties with Marchand's description of nitrosalicylic acid salts. When subjected to analysis, 0·1695 grm. of the silver salt gave

0.0630 grm. of silver, equal to 37.17 per cent.,

the quantity of silver in nitrosalicylate of silver being 37.24 per cent. When datiscine was allowed to stand in contact with dilute nitric acid in the cold it gradually dissolved, and the liquid assumed a yellow colour. The solution, when left to evaporate in vacuo, was found to contain a mixture of oxalic and nitropicric acids.

Action of Potash on Datiscine and Datiscetine.

It was stated in a previous part of this paper that datiscine and datiscetine dissolve in solutions of caustic alkalies without decomposition, and that datiscine, when boiled for some time, is decomposed with the formation of datiscetine. It only remained therefore to try the action of fused hydrate of potash. Datiscetine, when added in small successive portions to fused hydrate of potash, assumed a deep orange colour, and then dissolved with the evolution of hydrogen gas. When the disengagement of hydrogen ceased, the mass was dissolved in water and supersaturated with hydrochloric acid. A partly crystalline resinous substance separated, which, by sublimation, yielded perfectly colourless long crystals, closely resembling benzoic acid. Their solution in water assumed, on the addition of perchloride of iron, that deep violet tint which disappears on the addition of hydrochloric acid, and is characteristic of salicylic acid.

Action of Chromic Acid.

Datiscetine was likewise distilled with bichromate of potash and sulphuric acid; the liquid which came over did not contain oily drops, but had the smell of salicylous acid, and formed with persalts of iron a purple-coloured solution.

A trace of salicylous acid appeared therefore to have been produced.

It follows therefore, I think, from the experiment already detailed, that datiscine, like salicine, phloridzine, &c., is a glucoside, and that it approaches nearer to salicine than any other glucoside, with the exception of populine, yet known. In fact I am not aware of any glucoside, with the exception of salicine and populine, which, when treated with nitric acid, yields nitrosalicylic or even nitropicric acid. Phloridzine and phloretine, for instance, when treated with nitric acid, are stated by different experimenters to yield only oxalic acid. I repeated the experiment with phloretine, and obtained much oxalic acid, while the residual liquor yielded not a trace of chloropicrine when treated with hypochlorite of lime, and consequently contained no nitropicric acid. Quercitrine, when likewise treated with nitric acid, was also found

to yield, as RIGAUD states, only oxalic acid. I had no opportunity of trying esculetine, but it is stated by those who have investigated it to yield only oxalic acid.

I will conclude this account of datiscine by proposing the following practical application. As is well known, the colouring matter of madder when boiled with dilute sulphuric acid is changed into sugar and garancine, a new dye-stuff, which for many purposes is found superior to that originally present in the madder.

Within the last twelve months, Mr. Lieshing, by treating the colouring matters in weld and quercitron bark with dilute sulphuric acid, has resolved them into new colouring matters, which are but slightly soluble in water, and are found nearly three times more powerful as dye-stuffs than the original colouring matters from which they had been produced. As datiscine, when boiled with dilute sulphuric acid, undergoes a perfectly similar transformation, being resolved into sugar and datiscetine, which has a much higher colouring power than the datiscine which has produced it, I have not the least doubt that silk dyers, who may hereafter employ solutions of Datisca cannabina, will find it highly advantageous to convert their datiscine into datiscetine by boiling it with dilute sulphuric acid; as the process is an extremely simple one, and as the datiscetine, from its sparing solubility in water, can be very readily obtained in a state of comparative purity.

Ptychotis Ajowan.

The Ptychotis Ajowan is an umbelliferous plant, well known in India for its aromatic and carminative properties. Its seeds, which very much resemble in appearance those of the caraway, only being much smaller, have a very agreeable odour, resembling oil of thyme.

On distilling these seeds repeatedly with water, the essential oil is very easily obtained, amounting to between five and six per cent. of the weight of the seeds. This oil has a light brown colour, and possesses an agreeable aromatic odour. Its specific gravity is 0.896 at 12° C., and upon leaving the oil for some time in an open dish to spontaneous evaporation, the temperature at the time being comparatively low, large beautiful crystals were deposited, which on examination were found to be identical with the stearopten brought from India by the late Dr. Stocks, and described by me in a short notice published in the number of the 'Pharmaceutical Journal' for December 1854. When the crude oil is submitted to distillation, it begins to boil at 160° C., the thermometer rising rapidly to 174° C. The thermometer then rises to 220° C., and the oil which comes over at this temperature crystallizes on cooling. The residue, which does not immediately crystallize, on remaining at rest for some time, solidifies into a crystalline mass, the crystals having precisely the same form as those obtained by spontaneous evaporation, and amounting, in weight, to from one-third to one-fourth of the crude oil. As it seemed probable from these experiments, therefore, that Ptychotis oil, like many other essential oils, is a

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mixture of a liquid hydrocarbon and of a less volatile oxygenated stearopten, I proceeded to separate these compounds.

The Hydrocarbon.—The more volatile portion of the oil was redistilled, that part of it which boiled at 176° C. being separately collected. After having been dried with chloride of calcium, it was distilled over caustic potash. It was then repeatedly treated with sodium, and again cautiously rectified. The hydrocarbon thus obtained was perfectly colourless, refracted light strongly, and had a pungent, aromatic odour, quite dissimilar, however, from that of oil of thyme. Its boiling-point was found to be 172° C., a thermometer being placed in the vapour, and its specific gravity 0.854 at 12° C. The following analyses show that it is isomeric with oil of turpentine.

- I. 0·1280 grm. gave 0·4145 grm. carbonic acid and 0·1335 grm. water.
- II. 0.1765 grm. gave 0.5705 grm. carbonic acid and 0.1825 grm. water.

| Required. | | | Found | Found. | | | |
|------------|----|--------------|-------|--------|--|--|--|
| | | | I. | II. | | | |
| $C_{10} =$ | 60 | 88.23 | 88.31 | 88.15 | | | |
| $H_8 =$ | 8 | 11.77 | 11.59 | 11.49 | | | |

When the oil was treated with hydrochloric acid no crystalline compound was obtained, but a brown mobile liquid, having an agreeable smell similar to the oil itself.

The Stearopten.—I have already mentioned that the portion remaining in the retort from the distillation of the crude oil, solidified on cooling into a crystalline mass. When cautiously rectified it began to boil at 218° C., the thermometer, towards the latter part of the distillation, rising to 225° C., and even higher. The greater portion, however, came over at about 222° C. The first portion which came over was quite colourless, and had a mild aromatic smell, but the subsequent portions had a more pungent odour, and a yellowish colour. The more volatile and by far the larger portion of the distillate crystallized on cooling, especially when agitated, the crystals assuming a rhombohedral form. When it was kept quite quiet, however, it remained liquid for several days, but on being plunged into a freezing mixture it immediately solidified. The less volatile and more coloured portion of the distillate could not be made to crystallize, even when kept in a mixture of snow and salt. The form of the crystals, obtained by the solidification of the distilled stearopten, appeared at first sight to differ from that of the stearopten from India given me by Dr. Stocks; but, upon these crystals being dissolved in the hydrocarbon of the oil, they were obtained in forms precisely similar to those of the Indian stearopten. This was also the case when either the crude or the distilled crystals were deposited from their solutions in alcohol or ether.

Through the kindness of Professor MILLER of Cambridge, I am enabled to submit the following very accurate description and measurements of these crystals.

"The white crystals, which were the purer portions of the distilled stearopten, have the following figure and measurements:-

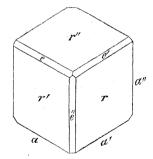
"Oblique:-Symbols of the simple forms:-

Angles between normals to the faces:-

"Rhombohedral:—Symbols of the simple forms, $a\ 01\overline{1}$, $r\ 100$, $e\ 011$.

Angles between normals to the faces:—

aa' 60 0 rr' 98 38 re' 49 19 ra' 40 41



- " Cleavage: -r very perfect. The faces e, a, are very narrow.
- "The white crystals are very thin in a direction perpendicular to the faces c. It is remarkable, that though they have the character of crystals of the oblique system, the cleavages make with each other very nearly the same angles as the cleavages of the brown crystals. The differences fall within the probable errors of observation: for the crystals, being very tender, and frequently having lost a portion of the original surface by evaporation, do not admit of very accurate measurement.
 - "In the brown crystals the cleavages are parallel to the faces r, r', r'', and the

[&]quot;Cleavage:—m, c very perfect.

[&]quot;The brown crystals.

angle between normals to rr' is 98° 38′. In the white crystals the cleavages are parallel to the faces c, m, m'. The angle between normals to m, c is 98° 40′, and the angle between normals to m and the face parallel to m' is 98° 42′. I should almost be inclined to suppose the brown crystals to have actually the same form as the white ones, the difference of the angles rr', r'r'', rr'' escaping observation, and as a consequence, that they have the same chemical constitution, a slight amount of impurity excepted."

The following are the results of the analyses of the stearopten obtained from different sources.

- A. Stearopten from India*.
- I. 0.2385 grm. gave 0.6955 grm. CO_2 and 0.2025 grm. HO.
- II. 0.3405 grm. gave 0.9910 grm. CO2 and 0.2815 grm. HO.
- III. 0.1870 grm. gave 0.5440 grm. CO2 and 0.1550 grm. HO.
- B. Stearopten obtained by the spontaneous evaporation of the oil. 0.3355 grm. gave 0.9780 grm. CO₂ and 0.2735 grm. HO.
 - C. Distilled stearopten recrystallized from the oil.
 - I. 0.2720 grm. gave 0.8015 grm. CO₂ and 0.2225 grm. HO.
 - II. 0.3115 grm. gave 0.9175 grm. CO2 and 0.2630 grm. HO.

The most simple formula agreeing with the numbers obtained by the above analyses is C_{10} H_7 O_7 as shown by the following Table:—

| Required. | Found. | | | | | |
|--|---------------------|---------------|-----------------------|---------------|---------------------|------------------------------|
| | Α. | | | В. С. | | Э. |
| $\begin{array}{cccc} C_{10} = 60 & 80.00 \\ H_7 = 7 & 9.33 \\ O = 8 & 10.67 \end{array}$ | I. 79·53 9·43 | 79·38 9·19 | 111. 79·34 9·19 | 79·50 9·06 | I. 80·36 9·09 | II. 8 0·33 9·38 |

- D. Analysis of the distilled stearopten not recrystallized out of the oil.
 - I. 0.4125 grm. gave 1.1885 CO₂ and 0.3375 grm. HO.
 - II. 0.3030 grm. gave 0.8655 CO2 and 0.2475 grm. HO.
- E. Analysis of the same crystals recrystallized out of ether and pressed between folds of blotting-paper.
 - I. 0.5915 grm. gave 1.7100 grm. CO₂ and 0.4860 grm. HO.
 - II. 0.2385 grm. gave 0.6900 grm. CO2 and 0.1975 grm. HO.

^{*} In the December Number of the 'Pharmaceutical Journal' for 1854 I published an analysis of the stearopten made from a small portion of the substance given me by the late Dr. Stocks. This I have subsequently found to be inaccurate, and the analyses given above are substituted in its stead.

F. Analysis of the last (now crystallizable) part of the distillation.

I. 0.3980 grm. gave 1.1195 grm. CO2 and 0.3395 grm. HO.

II. 0.3875 grm. gave 1.0930 grm. CO2 and 0.3225 grm. HO.

From the foregoing analyses the following per-centage results were obtained:—

| D. I | | G. | F. | | |
|-----------------------|---------------|---------------|---------------|---------------|---------------|
| I. | II. | I. | II. | I. | 11. |
| C = 78.58 H = 9.09 | 78·26 9·06 | 78·84 9·09 | 78·90 9·20 | 76·71 9·48 | 76·92 9·25 |

It will be seen, by the above analyses, that, during distillation, the stearopten undergoes partial decomposition, the amount of carbon being thus decreased.

The analyses D. and E. were evidently made with an impure substance, but the analysis F. agrees in a surprising manner with the numbers calculated from the formula C_{15} H_{11} O_2 , which requires

$$C_{15}=90$$
 76.92
 $H_{11}=11$ 9.40
 $O_{2}=16$

I do not however wish it to be supposed that the formula given above, or the double of it, viz. $C_{30} H_{22} O_4$, is the true formula for that substance; nevertheless I may observe that it bears a very simple relation to the formula of the stearopten itself. The one may be regarded as

$$3C_{10}H_6+4HO$$

and the other

$$3C_{10}H_6+3HO$$

that is, as two different hydrates of the same hypothetical hydrocarbon C_{10} H_6 , or C_{20} H_{12} , which perhaps might have been obtained by distilling the stearopten with anhydrous phosphoric acid.

All the experiments which I made, with a view of determining the basic or acid properties of the stearopten, gave negative results. When an alcoholic solution of the crystals was mixed with one of acetate of lead, no precipitate was formed, and the same was the case with nitrate and ammonio-nitrate of silver. The crystals of the stearopten dissolve when gently warmed in oil of vitriol, heat being evolved, and a purple colour produced. On standing the whole solidified, and the mass thus obtained was very soluble in water, yielding a colourless solution, with drops of a red oily liquid floating in it, produced probably by the action of the sulphuric acid on some of the hydrocarbon adhering to the stearopten. When dissolved in a small quantity of hot water the copulated acid was deposited, on the cooling of the solution, in fine colourless scaly crystals. I regret that the small quantity of the substance at my disposal prevented me from determining the equivalent of the stearopten by means of the acid or one of its salts. I obtained both the baryta and the lead salt in a crystallized

state by neutralizing the solutions of the acid with the carbonates of those bases. Their analysis, however, gave irregular results, as, owing to the smallness of their quantity, I could not prepare them in a state of perfect purity. In the former notice of the stearopten, already mentioned, it was stated that by long-continued digestion with concentrated nitric acid, the stearopten was dissolved, and a colourless crystalline acid produced. This acid is neither oxalic acid, nor, apparently, any of the nitrogenated acids. At least when warmed with hypochlorite of lime it gives off no chloropicrine. I suspect, therefore, that it will be found to be a new acid, the examination of which I hope ere long to lay before the Society. From the physical properties and the elementary composition of the stearopten of the Ptychotis Ajowan, it struck me that it was very similar to, if not identical with, the solid portion of oil of thyme, described by LALLEMAND in his recent papers on that substance*. This idea induced me to distil the stearopten dissolved in oil of vitriol with an excess of peroxide of manganese. As anticipated, besides formic acid, there came over yellow drops which solidified on cooling, forming large crystals, having a peculiar odour somewhat resembling iodine or kinone, and agreeing in every respect with the substance described by LALLEMAND as thymol.

Before Lallemand has published his experiments in detail, which are now only known from the two notes in the 'Comptes Rendus,' I do not think it possible to decide with perfect certainty whether thymol and the stearopten of the *Ptychotis* are really identical substances, and even then, perhaps, it will be found necessary to make more complete experiments with the stearopten of the *Ptychotis*. The hypothesis of their identity, however, appears to me highly probable from the great similarity existing in the most important properties of those substances. I may add, that I agree with Gerhardt in considering the crytallizable substance obtained by Arppe‡ from the essential oil of the Horse-mint (*Monarda punctata*, *huile de monarde*), to be identical with Lallemand's thymol and Doveri's § less volatile portion of the oil of thyme.

All these substances gave nearly the same numerical results when subjected to analysis.

Dover observed two boiling-points, one between 175° and 180° C., and the other between 230° and 235° C.

LALLEMAND found the boiling-point of his thymène to be 165° C., and obtained a liquid hydrochloric acid compound.

Arppe's crystallizable substance from the horse-mint oil, was found to melt at 48° C., to solidify at 38° C., and to boil at 224° C.

The crystals were rhombohedral, having one angle of 97° 30' and another of 82° 30'.

^{*} Compt. Rend. de l'Acad. xxxvii. 498, and xxxviii. 1022.

[†] Traité de Chimie Organique, iii. 610.

[‡] Annalen der Chemie und Pharmacie, lviii. 41; Chem. Gaz. December 1846.

[§] Annales de Chimie et de Physique, [3] xx. 174.

The Ptychotis oil, according to my experiments, contains a hydrocarbon boiling at 172°, and forming a liquid hydrochloric acid compound, and a crystallizable substance melting at 44°C., and boiling at about 222°C. The principal angles are stated by Professor MILLER to be—

 "Crystallized on cooling
 ...
 $rr' = 98^\circ$ 38

 Indian crystals
 ...
 ...
 mc = 98 40

 Indian crystals
 ...
 ...
 mm' = 81 18

 Indian crystals
 ...
 ...
 m'c = 81 20."

Two properties, however, I observed different from those given by LALLEMAND, viz. that the stearopten of the *Ptychotis* is precipitated (in a liquid state) from its alcoholic solutions by water, and that potash does not dissolve it, but merely causes it to assume the liquid state.

From the results of these experiments, therefore, I think we may confidently infer that the stearopten of the Ptychotis oil, and the crystallizable oxygenated portion of oil of thyme, examined by LALLEMAND, if not identical, as I apprehend they are, are certainly extremely similar bodies.

Gum of the Gardenia lucida, Roxb. (the Decamalee Gum of Scinde).

The specimen of this gum on which I operated was evidently very old. It formed a hard, dry mass, of a dark brown colour, with numerous patches of greenish-yellow matter disseminated through it. It had but a faint odour, unless freshly fractured or gently heated, when it smelt like the urine of the cat. A comparatively recent specimen of this gum, which I saw in the hands of the late Dr. Stocks, had nearly the consistence of candied honey, and an exceedingly offensive odour. Dr. Stocks informed me that the recent gum was employed as a dressing for wounds, as it kept off the flies.

The resin was digested in strong spirits of wine till a saturated solution was obtained. This, on cooling, immediately deposited some yellow, amorphous flocks. These were separated by filtration, and the clear liquid slowly evaporated in vacuo. On standing a few days, it deposited slender golden-yellow crystals, about half an inch in length. The crystals had considerable lustre, and were very brittle. To this crystalline substance I propose giving the provisional name of Gardenine.

inch in length. The crystals had considerable lustre, and were very brittle. To this crystalline substance I propose giving the provisional name of Gardenine.

Gardenine is nearly insoluble both in cold and hot water. It dissolves pretty readily in alcohol, but much less easily in ether, yielding bright yellow solutions, out of which it crystallizes on cooling. Alkalies, such as ammonia, do not appear to increase its solubility. It is slightly soluble in hot hydrochloric acid. Strong oil of vitriol dissolves gardenine in the cold with the production of a beautiful dark red colour. On adding water to this solution the gardenine is precipitated apparently unchanged. Its alcoholic solutions give no precipitates with ammonio-nitrate of silver, or with basic acetate of lead. When gardenine is digested with concentrated

nitric acid, it is rapidly decomposed, nitropicric acid, but apparently no oxalic acid, being produced.

Unfortunately, from the very small quantity of resin at my disposal, I was unable to prepare a sufficient amount of the gardenine, either to subject it to analysis, or to examine it more particularly. Dr. Royle has, however, already commissioned a large quantity of the resin from India, which I trust will ere long enable me to complete its examination.

Gardenine appears to belong to the tolerably numerous class of indifferent crystallizable resins, of which it is certainly one of the most beautiful.

St. Bartholomew's Hospital, November 14th, 1855.

Notes on Datisca cannabina, Ajowan and Decamalee Gum, received from Dr. Royle, March 12, 1856.

Ikl-beer, the stems and roots of Datisca cannabina.

"Datisca is found both in the Old and New World, existing in the latter in Pennsylvania. D. cannabina, so named from its great resemblance to the Hemp-plant, extends from the south of Europe and Asia Minor through Iberia to the valleys of the Himalaya. I have obtained it from Cashmere and Kunawm, and found it at the foot of the Choor and Kedarkanta mountains. It spreads also to Nepal; D. nepalensis, Don, being the same species."—Royle, Himal. Bot. p. 340.

The Ikl-beer is much esteemed in the Punjab for dyeing silk of a yellow colour. It is probable that some of the silk scarves of a lemon-yellow colour, which were much admired by artists for the delicacy of their colour, had been dyed by this substance, as it is there esteemed for dyeing silk of this colour.

stance, as it is there esteemed for dyeing silk of this colour.

Ajwain.

"The remaining Umbelliferæ, which are known in India, are those found only in a cultivated state; but this from so remote a period as to have become perfectly naturalized, and known to the natives, as well as to have names given to them in the languages of different parts of the country; some also have not as yet been found in other parts of the world;"—" as Ptychotis Ajowan, known everywhere by the name Ajwain, slightly varied in different districts."—" In addition to these, Ptychotis sylvestris, nob., called arub ajwain, is used as a carminative by the natives."—ROYLE, Himalaya Bot. p. 229.

"Dr. Roxburgh, in describing Ligusticum Ajowan, states, he cannot conceive that this famous Indian plant, aromatic in smell, pungent in taste, used both by natives and Europeans for culinary and medicinal purposes, can be unknown to European botanists. To Ajwain Persian authors assign nankhwah as the Arabic name. This is the size (Nankhwah) of Avicenna, written nanachua and nanachue in the marginal translation of Ammi, in the Latin edition of his works; which names are quoted under Ammi by Mathiolus, in his Commentaries on Dioscorides. But in Persian works on Materia Medica, Aammi is also given as the Greek synonym of nankhwah, that is, of Ajwain, which Dr. Roxburgh justly supposed could not be unknown to Europeans. This plant has been referred by M. DeCandolle to the genus Ptychotis, which brings it near P. copticum, called at one time Ammi copticum: the Ammi itself is called Cuminum Æthiopicum and regium; the latter name is translated by Kumoon Mullookee, and is given as a synonym of nankhwah in Persian authors."—L. c. p. 230. It is probable therefore that this Indian species of Ptychotis has long been employed as the Aammi of the Greeks.

Decamalee.

"This is the gum of the Gardenia lucida. It exudes in amber-coloured transparent drops, at the ends of the young shoots, and from thence is collected. It is most useful in preventing vermin from breeding in wounds. It is brought to Bombay from the interior."—Bombay List of Articles for Exhibition of 1851, p. 30.