reduction in the surface-tension, though the action may be a purely mechanical one.

I hope to continue and extend the experiments at an early date; meanwhile my thanks are due to Professor Tait for many valuable suggestions, and to Mr D. J. Graham who has assisted me in all the experiments.

The Absorption Spectra of Certain Vegetable Colouring Matters. By C. Michie Smith. (With a Plate.)

(Read March 17, 1890.)

For the substances dealt with in this paper I have been indebted at various times, to the kindness of Mr David Hooper, Quinologist to the Madras Government. The observations have been made with several instruments, but have all been reduced to the scale of the direct vision spectroscope of the Chemical Laboratory of the Edinburgh University, kindly placed at my disposal for the most important part of the work. The illumination used with this instrument is a 10-candle power incandescent lamp; with the other instruments sun-light was used. I have thought it better for practical purposes to draw the spectra to the natural scale of the instrument than to reduce them to a scale of wave-lengths, but data are supplied for finding the wave-length corresponding to any part of the spectrum. To represent the varying shades of an absorption spectrum is extremely difficult, and the results usually obtained are, at best, far from satisfactory. The method I have employed is to draw the spectra on a large scale, shading the various parts by aid of a light curve, and then reduce this drawing to the required size by photography. The result, though not all that could be desired, is fairly satisfactory.

Colouring Matter from Trichosanthes palmata.—Mr Hooper has given me the following notes on this substance:—"The plant which yields it is the *Trichosanthes palmata*, one of the Gourd tribe or Cucurbitaceæ, and the rounded scarlet fruits have their seeds imbedded in a green bitter pulp. The bitter principle is a glucoside, soluble in water and alcohol, and affords a red solution, changing to purple with sulphuric acid. I have named it 'trichosanthin,' as

it differs from colocynthin. The green matter is best prepared by agitating the dry pulp with ether, evaporating down and dissolving the ethereal residue in strong spirit. In this manner the bitter principle and fatty matters are eliminated." The solution closely resembles a solution of chlorophyll of equal strength. Both are beautifully dichroic, appearing green in thin, and red in thicker layers; both also have a red fluorescence. The chief difference on inspection is that a much thicker layer of chlorophyll is required to yield the red colour by transmitted light.

Spectrum.—The spectroscope at once shows that this green colouring matter is not chlorophyll. Spectra (a), (b), and (c), in the plate are for different thicknesses of the trichosanthes colouring matter, while (d) gives the spectrum of chlorophyll from cabbage of a thickness and strength corresponding as nearly as possible with (b). Taking this as the most characteristic spectrum, it may be thus described:—The spectrum begins at 1736, and slight shading continues to 1693. The first band begins (penumbra) at 1638 (W. L. 654.1), and ends about 1600 (W. L. 615), the maximum absorption being from 1631 to 1627, and from 1605 to 1602. From this there is a small amount of absorption till the second band begins at 1576 (W. L. 593.4), and continues to 1543 (W. L. 566.8), the maximum absorption being from 1570 to 1563. From this there is no perceptible absorption till the third band, which begins at 1516 (W. L. 548.4), and continues to 1495 (W. L. 534.8), the maximum darkness being from 1511 to 1501. There is a fourth band, very faint, with its centre about 1452 (W. L. 510.6), and a fifth extending from 1400 (W. L. 485) to 1371. The spectrum ends about 1355 (W. L. 467). The relative depths of the maxima of these five bands are 10, 5, 4, $1\frac{1}{2}$, 1. When a thin layer of the solution is used the spectrum shows two strongly marked bands from 1625 to 1612 (darkness 10), and from 1569 to 1550 (darkness 4), and a slight trace of a third band with its centre at 1501. The spectrum ends sharply at 1340. With a very thick layer the first band widens out in both directions, and strong absorption—sufficient to mask bands II. and III.—continues to 1485. There is also much increased absorption in the blue. How completely these spectra differ from that of chlorophyll will best be seen from the plate. The chief band of chlorophyll lies

between 1665 (W. L. 789) and 1625 (W. L. 639.8), while the chief band in a thin film of trichosanthes would almost exactly fill up the interval between bands I. and II. in chlorophyll. Bands III., IV., and V. of trichosanthes may be coincident with faint chlorophyll bands.

The positions of some of the chlorophyll bands, as is well known, can be changed by the action of reagents, and the trichosanthes bands are even more strongly affected. The first reagent experimented with was sulphide of ammonia, which probably has a reducing action. The result is shown in spectra (e), (f) and (g), which represent the appearance after 2, 11, and 39 days respectively, after which there was no further change. Figure (h) gives the spectrum of chlorophyll similarly treated. The change in the trichosanthes spectrum is complete. Band I. gradually becomes weaker, and finally vanishes; two new bands appear in the space between bands I. and II. of the original spectrum; band II. is apparently displaced towards the violet end and intensified; and band IV. is greatly widened. Chlorophyll is much less affected, and the difference between two spectra could hardly be more complete than that between (g) and (h).

When the original trichosanthes solution is treated with strong hydrochloric acid the spectrum consists of three principal bands. The first band begins (penumbra) 1606, and extends to 1576; the maximum absorption is from 1593 (W. L. 608.6) to 1576 (W. L. 593.4). From this there is considerable absorption to the second band, of which the maximum absorption extends from 1557 (W. L. 577.6) to 1532 (W. L. 558.8). Slight absorption continues to the third band, which extends from 1497 (W. L. 536) to 1467 (W. L. 519). The relative intensities of these three bands are about 8, 7, 4. These three bands may perhaps represent the three first bands of the natural spectrum moved by different amounts towards the more refrangible end. When this spectrum (i) is compared with the spectrum of chlorophyll similarly treated (j), it is seen that the three bands correspond with three of the chlorophyll bands, while there is nothing to represent the first and most prominent chlorophyll band. It is of importance to notice, too, that the unrepresented chlorophyll band is the one least affected by reagents.

Another difference between the trichosanthes colouring matter and chlorophyll is that when treated either with ammonia sulphide or hydrochloric acid the former ceases to be green in thin layers, while the latter ceases to be red in thick layers. The reason for this becomes at once plain when the spectra are examined. The question of the relation which the trichosanthes colouring matter bears to chlorophyll is one of considerable interest, for it is evident that there is some relation, since in the products of the action of hydrochloric acid there are three bands which are common to the two spectra. That they differ greatly is equally evident from the dissimilarity of the original spectra and of those got after acting on the solutions with ammonia sulphide. The trichosanthes colouring matter is found inside a thick opaque rind, and so has probably been formed in the dark, at least it cannot serve the purpose which chlorophyll serves in leaves. Chlorophyll, according to Sachs, is formed in complete darkness only in the cotyledons of some conifers and in the leaves of ferns; but etiolin, which in darkness usually takes the place of chlorophyll, has a spectrum which does not materially differ from the chlorophyll spectrum, and is certainly not the same as that under discussion. Chlorophyll itself is held by many who have studied it to be a mixture of several distinct colouring matters. Professor Stokes * finds that the chlorophyll of land plants is a mixture of four substances, two green and two yellow, three of which are easily decomposed by acids. I cannot find any account of the experiments from which this conclusion is deduced, nor any description of the spectra of the several constituents, but it seems probable that the first band in the red is that due to the constituent which is not easily decomposed by acids. Mr Sorby † holds that the chlorophyll of land plants is a mixture of two substances, which he calls "blue chlorophyll" and "yellow chlorophyll." To each of these he ascribes a single absorption band in the red; but the diagram which accompanies his paper is so unsatisfactory that it is impossible to identify these with bands in the natural chlorophyll spectrum, though presumably the first band in the spectrum is that due to his "blue chlorophyll." But this first band is quite unrepresented in the trichosanthes spectrum, so that it seems a fair conclusion that the

* *Proc. Roy. Soc.* xiii. 144.† *Proc. Roy. Soc.*, xxi. 451.

"blue chlorophyll" of Sorby, or one, perhaps both, of the green chlorophylls of Stokes, is absent from the trichosanthes colouring matter. Its place is taken by another substance which yields the first band, which is not coincident with any of the chlorophyll bands. This substance, unlike that yielding the first chlorophyll band, is very readily decomposed by acids, and is slowly decomposed by ammonia sulphide.

Bands II., III., and V. in the trichosanthes spectrum apparently coincide in position with bands III., IV., and V. of the chlorophyll spectrum. Of these latter III. and V. are not distinctly shown in the accompanying plate, but are obtained with a comparatively weak solution and a strong light. Band IV. of the trichosanthes spectrum is extremely faint. It is not, however, possible to lay much stress on the apparent coincidence of these bands, since their behaviour under treatment with ammonia sulphide is so very different. A comparison of spectra (*g*) and (*h*) shows that no two of the bands are even approximately coincident—in fact, the two spectra are almost complementary. On the other hand, spectra (*i*) and (*j*) show that after treatment with strong hydrochloric acid, there is almost perfect coincidence between three of the bands in the two spectra. The influence of hydrochloric acid on chlorophyll has been studied by many observers. Russell and Lapraik* consider that the change produced is simply a molecular one, and call the two forms α - and β -chlorophyll. Schunck, on the other hand, holds† that the change is a chemical one, and that the ultimate product is identical with Frémy's phyllocyanin. The latter view certainly seems to explain the observations best, and in accordance with it we may say that the trichosanthes colouring matter contains a substance which is not chlorophyll, but which on treatment with hydrochloric acid yields one of the constituents of phyllocyanin, which is itself probably a mixture of two substances. In chlorophyll a partial change is produced by a very weak acid, so that extracts of certain leaves, such as those of the Virginian creeper, yield the modified spectrum, unless care be taken to neutralise the acid before extracting the chlorophyll. It is possible that a somewhat similar change has been produced in the trichosanthes colouring matter by the trichosanthin which occurs along with it in the pulp.

* *Jour. Chem. Soc.*, vol. xli. p. 334. † *Annals of Botany*, vol. iii. p. 86.

Colouring Matter from Ventilago madraspatana.—Of this Mr Hooper writes:—"The red colouring matter in the other bottle should be more extensively known. It is a drug that has been used as a dye in South India for ages, under the name of 'Vembádam bark.' It is the produce of a large creeper, the *Ventilago madraspatana*, which grows on the slopes of the Nilgiris and in the Mysore district. The bark, besides dyeing silk and other materials, yields its colour to fixed and volatile oils, and, what is a desideratum, to kerosene oil. From an analysis, I make it an anthracene derivative." The absorption spectrum for thin and thicker films is shown in figures (*k*) and (*l*). There are no absorption bands, but the light is completely absorbed, even with a very thin film, except from 1730 to 1588 (W. L. 604). With a thicker layer the absorption is complete, except from 1702 (W. L. 743) to 1622 (W. L. 636·6). Thus the absorption is almost entirely confined to the more refrangible end. This substance would probably be found very suitable for dyeing cloths for use as non-actinic blinds in "dark rooms."

Colouring Matter from the Funiculus of the Wattle.—This yields a very pretty spectrum, figure (*m*), characterised by two well-marked absorption bands. The first extends from about 1546 (W. L. 568·8) to 1519 (W. L. 550·2), the second from 1506 (W. L. 541·8) to 1453 (W. L. 511·2). The relative darkness of the two bands is 10 : 8. When a thicker layer of the substance is used the two bands almost come together, but a slight green colour is seen between them. The absorption between band II. and the end of the spectrum also increases. In an alkaline solution the bands are somewhat narrower, but their centres are unchanged in position.

Solution of "Waras."—The dye known as "Waras" is got from the glands of the fruit of *Flemingia Grahamiana* (W. and A.), one of the Leguminosæ. The absorption spectrum shows no bands, but absorption is complete except between 1580 (W. L. 597) and 1523 (W. L. 552·8).

Solution of "Kamala."—This dye is got from the glands of the fruit of *Rottlera tinctoria*, one of the Euphorbiaceæ. It resembles Waras very closely, but is transparent to light of a somewhat greater wave-length. The absorption is complete except between 1688 (W. L. 722) and 1549 (W. L. 571·2). The chemical relations of

ABSORPTION SPECTRA OF CERTAIN VEGETABLE COLOURING MATTERS.

Original from 1890

Kamala and Waras have been examined by Mr D Hooper,* who shows that they are very similar, but not identical.

It is worth noting that of the colouring matters examined those giving definite absorption bands yield fugitive dyes, while the others yield permanent dyes.

My thanks are due to Dr J. Gibson for assistance received during the progress of the inquiry.

DESCRIPTION OF PLATE.

- (a) Colouring matter from *Trichosanthes palmata*, 0.5 cm. thick.
- (b) " " 2.0 cm. "
- (c) " " 4.0 cm. "
- (d) Chlorophyll from cabbage, 2 cm. thick.
- (e) Colouring matter from *Trichosanthes palmata* + ammonia sulphide after 2 days.
- (f) " " " 11 "
- (g) " " " 39 "
- (h) Chlorophyll + ammonia sulphide.
- (i) Colouring matter from *Trichosanthes palmata* + hydrochloric acid.
- (j) Chlorophyll + hydrochloric acid.
- (k) Colouring matter from *Ventilago madraspatana*, thin layer.
- (l) " " thick layer.
- (m) " funiculus of Wattle.
- (n) Waras.
- (o) Kamala.

On a Mechanism for the Constitution of Ether.

By Sir William Thomson:

(Read March 17, 1890.)

1. In a communication to the Royal Society of Edinburgh of 4th March 1889, I stated the problem of constructing a jointed model under gyrostatic domination, to fulfil the condition of having no rigidity against irrotational deformations, and of resisting rotation, or rotational deformation, with quasi-elastic force in simple proportion to rotation. I gave a solution, illustrated by a model, for the case of points all in one plane; but I did not then see any very simple three-dimensional solution. After many unavailing efforts I have recently found the following.

* *Pharmaceutical Journal*, vol. xviii. p. 213.