

subsidence, e.g. coral reefs and islands, are parts of the earth's surface which have lately increased rapidly in weight; and it may be worthy of consideration whether coral and volcanic islands have contributed to deepen the bed of the ocean.

J. F. ANDERSON

Cauterets, Hautes Pyrenees, July 12

Curious Rainbow

AN unusual atmospheric effect was witnessed here to-day, which I had a good opportunity of observing. The sun was about 8° from the horizon, shining brightly upon a heavy shower which had a background of dark clouds. The result was, of course, a double rainbow of remarkable brilliancy. In addition, however, to the ordinary circular and concentric bows, there was a third of an elliptical form, the two ends of which respectively sprang from the two ends of the inner arc, while the elliptical curve cut the outer arc at each extremity of a chord, which was parallel to, and which intersected the normal radius at a point about two-thirds of its length above, the diameter that formed the common base. The top of the elliptical bow was thus the outermost of the three, but the space between its inner margin and the outer margin of the second bow, although quite distinct, was not large.

The appearance of the third bow was due to light reflected from the sea. The sun being low, the resulting line of reflection was long, and it was the linear character of the source of light which gave the elliptical form to the bow it occasioned.

Dunskait, Ross-shire, July 10

GERGE J. ROMANES

CHLOROPHYLL COLOURING-MATTERS *

II.

I THINK there can be no doubt that the spectra of the various yellow substances given in Pl. II., Figs. 3, 4, and 6 of Dr. Kraus's work, are due to a variable mixture of xanthophyll, yellow xanthophyll, and lichnoxanthine. These can be separated, and do occur in different kinds of plants, either alone or mixed in such variable proportions that the spectra of the solutions show the absorption-bands, not only in variable positions, but also much less distinctly in some cases than in others. This difference is ascribed by the author, not to a variation in the relative proportion of two or more substances, each having definite and unvarying characters, but to the modification of one single substance, due to some unknown cause, assigning as a reason for this supposition that the chemical reactions are the same, and that the positions of the absorption-bands vary so gradually from one extreme to the other that no distinct demarcation can be detected. Now this is so very fundamental a question in such studies, and, according as it is decided, would modify the conclusions so much, that it is requisite to discuss it somewhat fully. No doubt the position of the absorption-bands seen in the spectra of solutions in different liquids does differ very considerably, but I feel persuaded that the spectrum of the same chemical compound, dissolved in the same liquid, is the same in all cases; and that, if there is any difference between the spectra of two similar solutions, it is due to a difference in the substances themselves. I would restrict the term *modification* to those changes sometimes produced by the action of weak alkalis or acids, or by deoxidizing reagents, which are only of a temporary nature, so that when the solution is restored to its original state, the spectrum is seen to be just as at first. We really do require such a term, and I have myself constantly used it in this sense. There is, however, no such relation between the different colouring-matters belonging to what I have called the xanthophyll group; and, though the presence or absence of oily substances may, and sometimes does, materially influence the position of the absorption-bands seen in the spectra of plants themselves, yet, when dissolved in a relatively large quantity of a solvent, this effect is altogether overcome. As I have shown in my late paper the position of the

* Continued from p. 204.

absorption-bands in the different members of the xanthophyll group is very different, and yet it would be easy so to mix them as to have a perfect series of connecting links, and in my opinion the variations from what appear to be independent compounds may be explained in an extremely simple and satisfactory manner, without supposing that the optical characters are subject to any such variations as are ascribed to them by the author. Whenever I have met with these variations I have looked upon them as presumptive evidence of there being a mixture, and have always been able to prove the truth of this principle by subsequent conclusive experiments. The following example will serve very well to explain my views. Many yellow flowers are coloured by a variable mixture of what I have called xanthophyll, yellow xanthophyll, and lichnoxanthine. The former occurs separately in the Alga, *Porphyra vulgaris*, the second in such pale yellow flowers as the yellow *Chrysanthemum*, and the last in the yellow fungus, *Clavaria fusiformis*. The absorption-bands of these two kinds of xanthophyll are in a very different position, and the lichnoxanthine gives no bands, only an uniform absorption, extending over about one half of the spectrum from the blue end. The chemical reactions are also equally distinct. On dissolving each in absolute alcohol, and adding a little hydrochloric acid, the first fades slowly, without being first changed into another yellow substance, and without turning blue or green; the second is first altered into another yellow substance, giving a spectrum with two absorption-bands in a different position, and then turns to a deep blue, whilst the last remains unchanged for a much longer time, and fades very slowly. Now, of course, if all these were mixed together in variable quantities, we should get results varying according to the relative amount of each. The absorption-bands due to the two kinds of xanthophyll would lie in an intermediate position, according to the relative amount of each constituent, and would be more or less indistinct, according as there was more or less of the lichnoxanthine; and on adding a little hydrochloric acid to the solution in alcohol the colour would turn to a more or less blue green, and subsequently fade to a pale or deeper yellow, according to the relative quantity of each constituent.

In order to make my meaning more clear, let us suppose that we were to take a mixture of equal quantities of xanthophyll and yellow xanthophyll. Using the notation I have so often explained in former papers, the centres of the absorption-bands of the spectra of a solution in bisulphide of carbon would then be—

Xanthophyll	6½	8
The above mixture	6¾	8½
Yellow xanthophyll	7	8¼

Now on exposing solutions of xanthophyll or yellow xanthophyll to the sun both fade, and if examined when very little colour was left undecomposed, the bands would be seen to be in the same position as at first, the solution being in fact just as if a large part of the colour had been removed, or as if it had been much diluted. In the case of the mixture this would not be the case. Xanthophyll is more rapidly decomposed than yellow xanthophyll, so that when very little colour was left the bands would be no longer in the original position, but in the same place as those of yellow xanthophyll, showing that a small quantity of this is left, when all the other has been destroyed. If some lichnoxanthine had been mixed with the solution, after longer exposure to the sun no absorption-bands would be seen, only the general absorption due to that substance. Moreover if we took equally deep coloured solutions in absolute alcohol of the same three different specimens, and added a little hydrochloric acid to each, the xanthophyll would fade till it was colourless, the yellow xanthophyll would turn to a fine blue,

and the mixture would also turn blue, but of only about half the depth of colour. If lichnoxanthine had been present it would have caused the colour to be green; and, after the blue product had faded, it would remain as a residual yellow. By experimenting with such known mixtures we therefore see that, independently of being able to partially separate the constituents, the evidence of the solution being a mixture consists in the difference in the position of the absorption-bands, in the change in their position, or disappearance, when partially decomposed by light, and in the relative quantity of blue substance formed by the action of hydrochloric acid, and of the residual yellow. Such, then, being the case, we know what kind of methods to employ in studying natural coloured solutions, suspected to be mixtures; and on applying them to the investigation of the solutions obtained from leaves and flowers, I find that they behave exactly like such artificial mixtures, and not only so, but there is generally no difficulty in more or less perfectly separating the constituents, so as to correspond more or less closely with the different substances in their more pure state. The evidence of their being mixtures is therefore as good as could be expected. Kraus seems never to have made such experiments, and yet he strongly criticises what I had said about the existence of several distinct kinds of xanthophyll; but I contend that by adopting the principles I have described, we can completely explain the various facts on perfectly simple principles, without supposing that the optical characters of any single substance are subject to variations from some unknown, and, as I believe, altogether imaginary cause.

The flowers of different varieties of *Eschscholtzia californica* are also a good illustration of my views. The very yellow petals are coloured by yellow xanthophyll, with a very little xanthophyll and lichnoxanthine, and thus correspond with many other similar flowers, but the more orange-coloured petals, and the orange-coloured portions of the yellower petals, contain in addition, another colouring-matter, giving the absorption-band in the green shown in Plate II. Fig. 7, at 1 a, of Kraus's work which, however, he did not look upon as evidence of a mixture—merely of what he calls a modification. Now, on exposing such a solution in bisulphide of carbon to the sun, this orange-coloured substance is more rapidly decomposed than the others, and in a while a yellower solution is left, which gives exactly the same spectrum as that due to the colouring-matter from the yellow petals. According to this view of the subject we therefore see that the yellow flowers are of the usual type, and that the more orange-coloured portions of the petals, and the whole of the orange-coloured varieties differ only in there being developed an unusual and independent substance, which in this case is of orange-colour, whereas in the flowers of some other plants, such additional colouring-matters are red or blue, as the case may be, and instead of being allied to xanthophyll, differ in almost every particular.

In conclusion I would say that the yellow colouring-matters, soluble in bisulphide of carbon, which exist in green leaves, are the above-named xanthophyll, yellow xanthophyll, and lichnoxanthine. This is probably the reason why this is also the normal type of yellow flowers, and why only in particular cases one or both of these substances are absent. To this I attribute the statement of the author that the chemical reactions are the same, for he has apparently never examined those plants which yield them in an approximately pure state.

In Pl. III. Fig. 2, Kraus gives a representation of the spectrum of a coloured solution obtained from certain species of *Oscillatoria*. This he has named *phycoxanthine*; but I am persuaded that the solution must have contained three perfectly distinct colouring-matters, which can be separated by chemical and photo-chemical methods, and do occur almost, or

quite, separately in other plants. For one of these substances I have adopted the author's name phycoxanthine. It may be obtained in the most pure state from the lichen *Peltigera canina*, when growing in such a damp and shady situation, that very little orange lichnoxanthine is developed. When dissolved in absolute alcohol and hydrochloric acid is added, it fades without turning blue. Another constituent of the mixture is what I have called *fucoxanthine*, which occurs quite free from phycoxanthine in *Fucus* and other olive *Alga*, and even in the same species of *Oscillatoria*, growing where there is very little light, as those which contain phycoxanthine, if growing well exposed to the sun. When dissolved in absolute alcohol and hydrochloric acid is added, it turns to a splendid blue. The third constituent of the mixed solution is what I have named *orange lichnoxanthine*, which can be obtained by itself from lichens, and is left when such a mixed solution as described by the author, in bisulphide of carbon, is exposed to the sun under green glass, until the phycoxanthine and fucoxanthine have been destroyed. When dissolved in absolute alcohol and treated with hydrochloric acid it fades very slowly. The relative amount of this is greatest in those specimens of *Oscillatoria* which grow very much exposed to the sun and air, and I have found by careful comparative quantitative analyses that the relative quantity of these various substances, which together constituted the author's phycoxanthine, varies in such a manner that, as far as the fundamental colouring-matters are concerned, the same or closely allied species of *Oscillatoria*, growing exposed to a varying amount of light, furnish a most interesting series of connecting links between olive *Alga* and lichens. When their vitality and constructive energy are very much reduced by want of light, their type of colouring closely approaches to that of olive *Alga*, whereas when they are exposed to much air and light, the type approaches to that of such lichens as *Peltigera canina*. I have met with other analogous cases, and if more extended research should still further confirm the existence of this analogy between the results due to abnormally reduced or increased vitality in the same kind of plants, and the normal characters of lower and higher classes of plants, it would certainly be remarkable, as showing that the vegetative energy of the lower classes is in some way or other of a lower type than that of the higher classes, and would present a striking analogy to the relation between the structure of animals whose development has been arrested, and that of those of lower organisation.

The fact of being able to prove that a coloured solution obtained from a plant is really a mixture of a number of different substances, may at first sight appear to be of very little consequence, but I trust that some of the conclusions deduced from this method of study will justify me in looking upon it as very well worthy of attention. When we come to study the various classes of plants growing under various conditions, with the view of constructing such a general science as that I have named comparative vegetable chromatology, these details become not only of the very greatest importance, but absolutely essential. By making qualitative and comparative quantitative analyses of the colouring-matters, carefully distinguishing the fundamental from the accidental, there seems every reason to believe that the petals and the foliage of plants can be brought into morphological agreement, and many of the leading classes of plants distinguished, and at the same time connected together, so as to form a continuous series, advancing from the lowest classes of animals to the highest classes of plants; whereas, if we were to look upon mixtures as independent colouring-matters, and were not to distinguish well-marked species, the whole vegetable kingdom would appear broken up and disjointed, without any chromatological continuity.

H. C. SORBY