# XI. *On some of the Substances contained in the Lichens employed for the preparations of Archil and Cudbear. By* EDWARD SCHUNCK, *Esq., Manchester.*

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OUR knowledge concerning that department of organic chemistry which embraces the colouring matters, and other principles nearly allied to them, is of the most imperfect kind. Though many other branches of organic chemistry have been so thoroughly and accurately investigated, that little or nothing remains to be known concerning them, this may be called an unexplored field. Most of the colouring matters are so little known, as regards even their most essential characters, as not to allow us either to justify or to question the propriety of throwing them together into one general class; a class distinguished from those nearly allied to it merely by the (as far as we know) adventitious circumstance of the substances belonging to it being endowed with certain more or less vivid colours. Among all the colouring matters there are none, the study of whose properties and reactions is calculated to throw more light on the nature of the whole class, than those which are prepared by an artificial process from certain kinds of lichens, and on this account it is desirable that they should be carefully examined. It was the circumstance of these substances being prepared artificially from plants perfectly devoid of colour that first attracted to them the attention of chemists, and led to a series of investigations by which a number of highly interesting substances was brought to light, and a process elucidated which belongs to the most remarkable and unparalleled in the whole range of organic chemistry.

Robiquet first discovered a colourless crystallizable substance in them (orcin), capable of being converted by the joint action of ammonia and oxygen into a true colouring matter, which contains neither the original substance nor ammonia as such. This interesting discovery was followed by others. The researches of Heeren made us acquainted with a series of substances contained in the *Roccella tinctoria*, possessed of the same property, and another substance, phloridzin, was shown by Stas to bear a complete analogy to orcin in this respect. The subsequent labours of Dumas, who subjected orcin and the bodies derived from it to an accurate examination, and of Kane, who has determined the composition of the substances discovered by Heeren, and of the colouring matters contained in archil and litmus, seemed to have sufficiently elucidated the subject. Some obscurities, however, in a part of Dr. Kane's late paper seemed to make it desirable that some of his results should be confirmed before being finally adopted, and at the suggestion of Professor Liebig I undertook the re-investigation of this subject, and performed it in his laboratory.

Instead of the *Roccella tinctoria* I employed in my experiments the lichens that grow on the basalt rocks of the Vogelsberg in Upper Hessia, where they are collected for the purpose of preparing a dye from them. These lichens were all crustaceous and belonged to the genera *Lecanora*, *Urceolaria*, *Variolaria*, &c. From them I extracted the following substances:—

1. A white crystalline substance, soluble in alcohol and æther but insoluble in water, bearing in its properties great resemblance to the substance called by Heeren *Erythrin* and by Kane *Erythrilin*, but different in composition, and giving other products of decomposition. This substance I call *Lecanorin*.

2. A crystallizable substance identical in properties and composition with Heeren's *Pseuderythrin* and Kane's *Erythrin*.

3. A fatty substance of acid properties, soluble in alcohol but insoluble in æther and water.

The method by which these substances were extracted and separated from one another, was the following. The lichens were reduced to a coarse powder and then treated with æther, in an apparatus of displacement, until the æther dissolved nothing more. The æthereal extract, which had acquired a green tinge from chlorophyll in solution, was distilled off, leaving as a residue a greenish yellow mass, consisting for the greater part of lecanorin. This mass was brought into a glass funnel and washed with small quantities of æther, until it had lost its green colour in part. It was then treated with boiling water in order to remove every trace of pseuderythrin, and, lastly, purified by dissolving it in a small quantity of boiling alcohol, which deposited on cooling a snow-white crystalline mass, consisting of lecanorin in a state of purity. The dark green æthereal fluid obtained by washing the impure lecanorin, contained besides lecanorin the greatest part of the pseuderythrin which had been extracted by the æther. The fluid was evaporated to dryness and the residual mass treated with boiling water, which deposited on cooling a mass of shining plates and needles of pseuderythrin, which was purified by re-crystallization. More of this substance was obtained by treating the lichens, which had been exhausted with æther, with boiling alcohol and filtering rapidly. The alcohol was distilled off and the residue treated with boiling water, which dissolved all the pseuderythrin and deposited it on cooling. The mass left undissolved was washed with æther, which dissolved all the chlorophyll and left behind the fatty substance mentioned above, which was purified by re-dissolving in alcohol.

I will now proceed to a more minute description of the properties of these several bodies.

### *Lecanorin.*

This substance, when pure, is perfectly white. If prepared in the manner described above, it has the appearance of a white mass composed of acicular needles. When its solutions are slowly evaporated, it crystallizes in silky needles grouped together in star-shaped masses. It is insoluble in boiling water, but soluble easily in alcohol and æther. Its solutions redden litmus paper. It is soluble in alkaline liquors, from which it is precipitated unchanged by acids, provided the solutions be not boiled and be not left to stand too long. It is insoluble in all weak acids, with the exception of acetic acid. Strong nitric acid converts it ultimately into oxalic acid. It combines with metallic oxides by double decomposition. Heated on platinum foil it melts, emits a dense vapour, and burns off, leaving but little carbonaceous residue. When heated in a tube closed at one end, it melts, and, under violent ebullition, gives off a dense vapour, which condenses in the upper part of the tube into a thick liquid, which after some time solidifies, forming a crystalline mass. The nature of this sublimate will be explained further on.

The action of the alkalies on this substance is of course the most interesting point connected with its history. A solution of lecanorin in ammonia when exposed to the air, acquires after some time a beautiful deep purple colour: from this solution acids precipitate a red colouring matter. A solution in potash, under the same circumstances, becomes of a deep red colour. Being desirous of ascertaining whether the lecanorin was immediately converted into the red colouring matter, or whether it passed first through any intermediate state, which was not improbable, I dissolved some of the substance in ammonia, excluding the solution from contact with the air. After a lapse of some hours, the solution, though perfectly colourless, was found no longer to contain any lecanorin; for acids, instead of producing a thick gelatinous or flocculent precipitate, as they do when applied immediately after solution has been effected, merely caused a brisk effervescence of carbonic acid, plainly showing that the substance had been completely decomposed without a colouring matter having been formed. The same effect was brought about instantaneously when the solution was boiled. In order to observe the process more clearly, I dissolved a quantity of lecanorin in baryta water in the cold. The solution, on being boiled or allowed to stand, deposited a great mass of pure carbonate of baryta. The liquid was filtered rapidly, and the excess of caustic baryta precipitated by a stream of carbonic acid: on slow evaporation it yielded large prismatic crystals of a substance which possessed characters in every respect identical with those of *orcin*. It had an extremely sweet taste, was capable of being volatilised without change and without leaving any residue, gave a deep blue colour when dissolved in ammonia and exposed to the air, struck a blood-red colour with nitric acid, and precipitated a solution of basic acetate of lead. Lecanorin thus is converted by the action of alkalies into orcin and carbonic acid, in the first instance, this decomposition always preceding the formation of colouring matters. The same decomposition is produced by the carbonated alkalies, by long boiling with water and by dry distillation, the heavy vapour mentioned above as being produced by heating lecanorin to decomposition, being vapour of orcin.

The composition of lecanorin is expressed by the formula $C_{18} H_8 O_8$. The results of the combustions which I made of it admit of no other interpretation. All attempts to determine its atomic weight by means of combining it with metallic oxides, failed. These compounds can only be prepared by double decomposition; but the facility with which lecanorin is decomposed when alkalies are added to its solutions, always renders the purity of the compounds formed liable to doubt. The compound with oxide of silver, formed by adding nitrate of silver to an alcoholic solution of lecanorin, and then precipitating by means of a few drops of ammonia, though it changed colour but slightly in drying, gave no consistent results. The compound with oxide of lead, formed by precipitating a solution of lecanorin with basic acetate of lead, was so basic and its formula so unusual, that I am led to suppose that one or two atoms of basic acetate of lead were precipitated together with it. By decomposing, however, a weighed quantity of lecanorin with caustic baryta, and determining the quantity of carbonate of baryta formed, I obtained very accurate results, confirming the formula $C_9\,H_4\,O_4$, or $C_{18}\,H_8\,O_8$, for lecanorin. In regard to the composition of orcin, I have been induced to replace the generally received formula for its composition by a new one. Dumas's formula for anhydrous orcin is $C_{18}\,H_7\,O_3$, and for crystallised orcin $C_{18}\,H_{12}\,O_8$, which evidently cannot be brought into accordance with the formula for lecanorin as given above. If, however, the formula $C_{16}\,H_6\,O_2$ be taken for anhydrous orcin, and $C_{16}\,H_{11}\,O_7$ for crystallized orcin, then the decomposition which lecanorin undergoes with alkalies may be expressed as follows:—

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| 1 atom of anhydrous orcin . . | $C_{16}\,H_6\,O_2$ |
| 2 atoms of water . . . . . . . | $H_2\,O_2$ |
| 2 atoms of carbonic acid . . . | $C_2\quad O_4$ |
| 1 atom of lecanorin . . . . . . | $C_{18}\,H_8\,O_8$ |

Two atoms of water are furnished by the decomposition of the lecanorin itself, and three more by the fluid, to form from $C_{16}\,H_6\,O_2$ one atom of crystallized orcin, $C_{16}\,H_{11}\,O_7$. The combustions which I have made of this substance agree perfectly with these formulas, but Dumas's analyses of the lead compound of orcin, which I have myself not yet examined, do not coincide with them, unless it be supposed that this compound contains acetate of lead, either in chemical combination or mechanically mixed.

In regard to the numerical results from which the above formulas have been deduced, I shall reserve them for a future occasion, when, having completed the investigation of the whole class of substances of which those here described are only a part, I shall be able to enter more minutely into details, and exhibit the facts and numbers brought to light in their proper connexion and order. I have merely been desirous of showing, on the present occasion, that our knowledge of this series of bodies is far from being complete. I have shown above, that the action of alkalies on lecanorin is twofold; it consists, first, in abstracting from the substance carbonic acid, a process not requiring the co-operation of the oxygen of the atmosphere; secondly, in inducing in contact with the air the formation of colouring matters. The first action seems to have been overlooked in the case of all the bodies nearly allied to lecanorin. I have found the most complete analogy in the case of Heeren's pseuderythrin; and, if I am not mistaken in the interpretation of his statements, his erythrin also undergoes the same decomposition as lecanorin, for the former is converted into erythrin-bitter by the very same agencies by which lecanorin is converted into orcin, and in fact there is the same relation in regard to all general properties between erythrin and erythrin-bitter as between lecanorin and orcin. This circumstance is of some importance, for in order to arrive at a knowledge of the exact composition of such complex bodies as the colouring matters formed by the action of alkalies on these substances, and to understand perfectly the nature of the process by which they are produced, it is absolutely necessary to know the exact substance out of which each is in the last instance formed, the last link of the chain which precedes its formation.

### *Pseuderythrin.*

For this substance it would be advisable to substitute another name, as in this case the substance by which it is accompanied is not erythrin but lecanorin. It is contained in very small quantities in the lichens that I examined. It is sparingly soluble in cold water, but easily soluble in boiling water, from which it crystallizes on cooling in shining plates and needles. If more of the substance is taken than the boiling water can dissolve, the part left undissolved melts and collects at the bottom of the fluid in oily drops, which, on the temperature falling a little below 212°, congeal and form crystalline masses. This is a characteristic property of pseuderythrin, and one distinctly mentioned by Heeren. It is easily soluble in alcohol and æther, and also in alkaline solutions. It gives compounds with metallic oxides by double decomposition. When dissolved in ammonia and exposed to the air, it gives, like lecanorin, a red colouring matter; but its conversion into the latter is much more slowly effected than that of lecanorin. When subjected to dry distillation it also gives a crystalline sublimate, accompanied by a copious disengagement of gas. When its solution in an alkali is boiled or left to stand some time, it imparts carbonic acid to the alkali, the decomposition being accomplished, however, with much more difficulty than with lecanorin. The exact nature of the substance left in solution after this decomposition I was unable to determine, on account of the very small quantity of pseuderythrin which I had at my disposal.

The combustions which I made of this substance confirmed the formula established by Liebig at the time of Heeren's investigation, viz. $C_{20}\ H_{12}\ O_8$.

The *fatty substance* mentioned above I have examined but slightly. It is soluble in alcohol, but insoluble in æther and water. From an alcoholic solution it is deposited in small pearly-white scales; if the solution be spontaneously evaporated, it is obtained in small, hard, shining, transparent crystals. It is soluble in alkalies, forming soapy solutions, and is re-precipitated by acids. Its alkaline solutions do not become coloured when exposed to the air. It cannot be melted without being decomposed.