XVIII. On the Constitution of the Resins. Part III. By James F. W. Johnston, Esq. M.A., F.R.S., Professor of Chemistry and Mineralogy in the University of Durham.

Received June 11,—Read June 20, 1839.

## VI. Resin of Sandarach.

THE resin of sandarach dissolves readily in alcohol, giving a yellow solution, which may be obtained of the consistence of a balsam. It dissolves without appreciable residue.

If this solution be largely diluted with alcohol, a white flocky resin separates in small quantity, falls slowly to the bottom, and may be procured in a state of considerable purity by decantation and washing with cold alcohol.

If to the alcoholic solution solid caustic potash, or a concentrated solution of this alkali in water be added, a precipitate falls, which re-dissolves if the potash be present in great excess. By adding, to a solution containing potash in excess, a solution of the resin as long as any precipitate falls, the whole of the resin thus separable may be thrown down. It may be washed by affusions of hot alcohol, by which a portion of it is dissolved; and the alcohol it holds apparently in combination, may be separated by heating for a sufficient length of time at a temperature not exceeding 250° FAHR.

- I. Resin A. of Sandarach.—The white flocks which fall to the bottom of the solution of sandarach resin in alcohol, being collected on the filter, washed with alcohol, and afterwards boiled in water, are obtained in the form of a white powder, having neither taste nor smell. Dried at 212° Fahr. this resin undergoes no change; but if the temperature be raised to about 300° Fahr., it gradually assumes a yellow colour, and slightly coheres, but does not melt. If the heat be still increased, the colour becomes brown, apparently indicating incipient decomposition.
  - 1. Of a portion of the resin thus obtained, and heated till it became yellowish,
    - A. 11.175 grains gave  $\ddot{C} = 31.70$ ,  $\dot{H} = 9.86$ .
    - B. 11.095 grains gave  $\ddot{C} = 31.315$ ,  $\dot{H} = 9.818$ , or per cent.,

$\Lambda$ .	В.
Carbon $= 78.437$	78.043
Hydrogen = 9.803	9.832
Oxygen $= 11.760$	12:125
100	100

2. Of a portion obtained by the same method from a second quantity of the crude resin, and well washed,

11.802 grains, heated till it acquired a tinge of yellow, gave  $\ddot{C}=33.06,~\dot{H}=10.53,$  or, per cent.,

Carbon = 
$$77.456$$
  
Hydrogen =  $9.913$   
Oxygen =  $12.631$   
 $100$ 

This analysis, which only the loss of the remainder of my resin by an accident prevented me from repeating, agrees with the formula  $C_{40}$   $H_{31}$   $O_5$ , which gives

	Calculated.		By experimen	nt.
		First p	ortion.	Second.
40 Carbon =	3057.480 = 77.515	78.437	78.043	77.456
Hydrogen =	386.867 = 9.808	9.803	9.832	9.913
Oxgen =	500.000 = 12.677	11.760	12.125	12.631
	3944:347 100	100	100	100

There can be little doubt, therefore, that the sparingly soluble resin of sandarach contains five of oxygen to forty of carbon; and as more care was taken to purify by washing with alcohol the portion which gave the result in the last column (2.), the true formula is most probably that above given,  $C_{40}$   $H_{31}$   $O_5$ .

II. Resin B. of Sandarach.—The alcoholic solution from which caustic potash ceased to throw down any precipitate was decanted, and a portion of the alcohol separated by distillation. It was then largely diluted with water, by which it was only slightly troubled; the resin was precipitated by muriatic acid, collected on the filter, and washed by repeated affusions of hot water. After drying at 212° Fahr. this resin was wholly dissolved by common alcohol in the cold. According to Unver-DORBEN the resin of sandarach consists of three resins, one thrown down from the alcoholic solution of the crude resin by caustic potash, the resin C. of Unverdorben and of the present paper, and two which remain in solution unaffected by the potash\*. When these mixed resins are separated from the potash by muriatic acid, in a way similar to that above described, he states that boiling alcohol dissolves the one and leaves the other. In my experiments, as above detailed, cold alcohol and cold ether also dissolved the whole of what I supposed to contain two resins; while from the solution of the crude resin, by simple dilution a precipitate fell, not noticed by Un-VERDORBEN, and possessing characters different from those exhibited by any of the three resins described by that experimenter.

Evaporated and heated at 212° Fahr., as long as any apparent change was produced, the alcoholic solution gave a bright yellow resin, brittle when cold, but softening at the temperature of boiling water.

<sup>\*</sup> Thomson's Organic Chemistry, p. 529.

A. 10.407 grains of it in this state gave  $\ddot{C} = 28.83$ , and  $\dot{H} = 9.40$ .

As this does not give a formula containing  $C_{40}$ , I exposed the resin dried in mass at  $212^{\circ}$  Fahr. to a higher temperature, when it melted, and frothed up, giving off vapours. To obtain it free from water and any other volatile substances it might retain, I evaporated a second portion of the alcoholic solution, and kept the resin in the state of a thin film for forty-eight hours at  $200^{\circ}$  Fahr.

B. 10.515 grains now gave  $\ddot{C} = 28.58$ , and  $\dot{H} = 9.295$ .

Still further heated for twenty hours at 250° Fahr., the resin was yellow and brittle, and

C. 11.69 grains gave  $\ddot{C} = 32.055$ , and  $\dot{H} = 10.22$ .

These three results are equal respectively to

Dried in mass at 212°.	In a thin film.  At 200° for 48 hours. Further 20 hours at 250° Fahr.	
Died in mass at 212.		
Carbon = 76.601 Hydrogen = 10.038 Oxygen = 13.361	75·08 9·82 15·10	75·82 9·71 14·47
100	100	100

The analyses B. and C. agree very closely with the formula  $C_{40}$   $H_{31}$   $O_6$ , which gives

Carbon = 
$$75.59$$
  
Hydrogen =  $9.56$   
Oxygen =  $14.85$ 

The slight excess of carbon in the third analysis, if not an error of experiment, indicates that the heating had been carried a little too far; while the similar excess both of carbon and hydrogen in the resin dried only at 212°, would imply the presence of a volatile carbo-hydrogen, which is wholly expelled only after long-continued heating. A familiar example of the presence of such a volatile compound, we have in the association of oil of turpentine with common resin; and the fact that most of the resins yield on distillation with water a volatile oil, gives ground for believing that the presence of substances analogous to oil of turpentine may tend more or less to modify or vitiate the results obtained by the analyses of resinous bodies, when sufficient precautions are not taken to ensure their expulsion.

III. Resins precipitated by Caustic Potash.—The precipitate thrown down by caustic potash from the alcoholic solution of the sandarach of commerce, dissolved readily in a hot dilute solution of caustic potash. From this solution largely diluted with water, the resin was precipitated by dilute muriatic acid, and afterwards washed on a filter till it ceased to render the water acid. Being then boiled in water, dried at 212°, and digested with boiling alcohol, only a small quantity was taken up. The

solution on evaporation gave a pale-yellow resin which did not fuse at 250° Fahr., but cohered at 300° Fahr.

A. 10.817 grs. gave 
$$\ddot{C} = 29.875$$
, and  $\dot{H} = 9.59$ .

As this *first* solution was likely to contain a portion of the more soluble resin B. carried down by the insoluble potash salt, when precipitated from the solution of the crude resin, the undissolved portion was boiled in a second and third quantity of alcohol. This third solution was evaporated, and the pale-yellow resin heated to 230° Fahr. for forty-eight hours.

B. 8.3 grs. gave 
$$\ddot{C} = 23.1$$
, and  $\dot{H} = 7.45$ 

These two analyses are equal to

Carbon = 
$$76.37$$
 B.  $76.95$  Hydrogen =  $9.85$  9.97 Oxygen =  $13.78$   $13.08$   $100$ 

The result of the first analysis is intermediate between those obtained from resins A. and B., the second which certainly represents the constitution of a purer form of the resin, approaches very nearly to the constitution of resin A. represented by the formula  $C_{40}$   $H_{31}$   $O_5$ .

It would appear, therefore, that one resin A. is to a certain extent soluble in an alcoholic solution of B., but that in some of the varieties of sandarach the quantity of A. actually present is greater than can be thus taken up, in consequence of which a portion sometimes remains behind undissolved when the natural resin is digested in cold alcohol. On treating with caustic potash, however, resin A. is wholly, or more correctly, perhaps almost entirely thrown down along with another resin C. and a small adhering portion of B. On decomposing this potash salt, as above described, with muriatic acid, the mixed resins are obtained and may be separated by boiling alcohol. Resin A. and the small quantity of B. are dissolved, giving a brownish yellow solution, from which on cooling, A. is in a great measure precipitated. Resin C. remains behind of a brown colour. After boiling in distilled water it is obtained in the form of a grey friable mass, which becomes yellowish when heated for twenty-four hours at 250° Fahr., but does not melt. At 500° Fahr. it melts into a brown semifluid mass, and speedily decomposes.

IV. Resin C. of Sandarach.—The mixed resins obtained from the potash salt by muriatic acid were boiled in repeated portions of common alcohol as above described. The insoluble portion was, in the hot alcohol, soft, glutinous, and of a brown colour. It was boiled in water, by which it was freed from alcohol, becoming hard and friable. Dried at 250°, it was in the state of a yellow powder.

A. 7.044 grs. burned in the air left 0.114 grs. of a grey residue, chiefly carbonate of lime, or 1.61 per cent.

B. 8.97 grs. gave 
$$\ddot{C} = 24.405$$
, and  $\dot{H} = 7.614$  grs. C. 9.08 grs. gave  $\ddot{C} = 24.46$ , and  $\dot{H} = 7.52$  grs.

corrected by A. these two analyses give

•	В.	С.	$(C_{40}H_{30}O_6)$ gives
Carbon	75.59	75.53	75.83
Hydroger	9.47	9.35	9.28
Oxygen	14.94	15.12	14.89
	100	100	100

It is remarkable, if the experiments above detailed are to be depended upon, that the only difference in constitution between resins B. and C. consists in the presence in the former of thirty-one, and in the latter of only thirty equivalents of hydrogen, while their respective solubilities in alcohol, their fusibilities and general relations to heat are so very dissimilar. We know as yet too little of their several relations to other substances to enable us to speculate on the mode in which the elements are grouped in the two compounds.

Conclusions.—The sandarach of commerce consists of three resins, all of which possess acid properties.

- 1.  $A = C_{40} H_{31} O_5$  a white or yellow powder, sparingly soluble in alcohol, more so in boiling than in cold, melting with difficulty, and decomposing at a temperature little above that at which it melts, existing in sandarach only in a small proportion, and partly separated on treating the natural resin with a large quantity of alcohol, and partly thrown down from this solution of the natural resin by caustic potash along with the insoluble resin C.
- 2. Resin B =  $C_{40}$   $H_{31}$   $O_6$  bright-yellow, brittle, softening at 212° Fahr., having the resinous odour of sandarach, dissolving largely in cold alcohol, constituting at least three-fourths of the natural resin, and remaining in solution when A. and C. are precipitated by caustic potash.
- 3. Resin  $C = C_{40} H_{30} O_6$  a pale-yellow powder, nearly soluble in boiling alcohol, requiring a high temperature to melt it, and at the same time undergoing decomposition. It exists in sandarach in much larger quantity than resin A., and is obtained in a pure state by decomposing with muriatic acid the precipitate thrown down by caustic potash, and boiling first in water and afterwards in repeated portions of common alcohol.

I shall have occasion hereafter to describe several other nearly insoluble resins, differing in composition from those above described, but I may here introduce the remark, that we are already prepared to anticipate unlike *rational* formulæ for the soluble and insoluble resins; since the number of atoms of oxygen contained in our *empirical* formulæ appear to have no relation to these properties of solubility and

fusibility. This is strikingly shown in the case of the resins above described, and there are many others in which this fact is equally apparent.

Note.—The disagreement between some of the details of the above examination of the resin of Sandarach, and those of Unverdorben, to whom we are indebted for the only previous methodical examination of a large number of the resins, is to be ascribed chiefly I believe to the mode in which Unverdorben examined the resins. Being unable to have recourse to the ultimate analysis of the substances he obtained, he distinguished them chiefly by their physical characters, which in many cases are very fallacious. It is possible, however, that different specimens of the resin may contain the several resins in different proportions.

## VII. Resin of the Pinus Abies or Spruce Fir, sometimes called Thus, or Common Frankincense.

This resin is brittle but soft, and easily scratched by the nail; of a pale-yellow colour, and semitransparent. It occurs in rounded masses of various sizes, mixed with chips of wood. When melted in hot water and strained through a cloth, it forms the Burgundy pitch of commerce. In cold alcohol it dissolves readily, leaving a variable proportion of a second resin B. in pure white opaque masses. This second resin is not insoluble in the cold, but only more sparingly soluble than resin A, and readily dissolves in hot alcohol. It should therefore be washed with several affusions of cold alcohol, and dried by strong pressure between folds of bibulous paper. Thus obtained and dried it is in the form of a white farinaceous powder, which requires a temperature of  $300^{\circ} + Fahr$ . to bring it into complete fusion; and on cooling from fusion it is pale-yellow, transparent, and brittle, differing little in appearance from resin A. after it has been similarly fused.

I. Resin A.—The solution of the soluble resin was evaporated, and exposed in a thin film for thirty-six hours to a heat not exceeding 200° Fahr.; it was still soft at that temperature, and on cooling became brittle, but did not contract and crack. In this state,

A. 12.288 grains gave  $\ddot{C}=33.67$ , and  $\dot{H}=10.35$  grains.

A portion of the resin thus analysed was again heated in a thin film for eighteen hours at a similar temperature. It was still beautifully transparent and pale-yellow, and on cooling contracted and cracked in various directions. In this state,

B. 11.63 grains gave  $\ddot{C} = 31.98$ , and  $\dot{H} = 9.731$ .

Another portion of the alcoholic solution was evaporated and heated as before for a still longer continuance, and to a temperature a little higher. It began now to assume a reddish tinge on the surface, and, on cooling, the fissures which traversed the yellow mass were of a beautiful red colour. Again analysed,

C. 12.35 grains gave  $\ddot{C} = 34.083$ , and  $\dot{H} = 10.238$ .

These three analyses are equal respectively to

Α.	В.	C.
Carbon $= 75.76$	76.01	76.31
Hydrogen = 9.35	9.29	9.21
Oxygen $= 14.89$	14.70	14.48
100	100	100

I consider the state of the portion employed for the second analysis B. to represent most nearly the normal condition of the resin, and the result of this analysis agrees almost exactly with the formula  $C_{40}$   $H_{29}$   $O_6$ . Thus

The results of the whole three analyses are very near these calculated numbers, and yet they illustrate very distinctly what I have frequently had occasion to remark in the study of the resins, that we can rarely depend on the results of any one analysis, however carefully performed. To obtain the resin in a normal state, free on the one hand from adhering water, alcohol, or ether, and on the other from any carbo-hydrogen or other compounds which may be present in it in its natural state, it must be heated for a length of time, and yet neither so long nor to so high a temperature as to induce incipient decomposition. Much attention therefore is required to the process of heating; and when this attention is paid, some change of appearance will always be observed which may be presumed to indicate decomposition; still where doubt remains, or where a formula cannot be obtained, a series of analyses of the resin, in its several stages of heating or drying, can alone determine what numbers are to be considered as expressing most nearly its true elementary constitution.

- II. Resin B. of the Pinus Abies.—I have already stated that cold alcohol leaves undissolved a white opake portion, in greater or less quantity, when the natural resin is digested in this liquid. By repeated solutions in hot alcohol, partial evaporation, and pressure between folds of bibulous paper, this resin may be obtained nearly free from the more soluble resin A. The three portions subjected to analysis were prepared from as many separate quantities of the natural resin, and the constancy of the results may be considered as indicating the degree of confidence to be placed in the formula deduced from them.
- A. 12.247 grains heated till it was completely melted and began to assume a reddish hue, gave  $\ddot{C} = 34.35$ , and  $\dot{H} = 10.37$  grains.
- B. 11.94 grains heated only till it cohered, and was brittle when cold, gave  $\ddot{C} = 33.767$ , and  $\dot{H} = 10.42$  grains.
  - C. 8.495 grains after perfect fusion gave  $\ddot{C} = 24.02$ , and  $\dot{H} = 7.18$  grains.

These results are equal to

And they indicate the formulæ C<sub>40</sub> H<sub>29</sub> O<sub>5</sub>, which gives

Carbon = 
$$77.95$$
  
Hydrogen =  $9.30$   
Oxygen =  $12.75$ 

Conclusions.—The resin of the Pinus Abies, therefore, consists of two acid resins, represented respectively by

 $A = C_{40} H_{29} O_6$ , easily soluble in cold alcohol, fusible about 212° FAHR.

 $B = C_{40} H_{29} O_5$ , sparingly soluble in cold alcohol, fusible at 300° Fahr.

The presence of a second and crystallizable resin in this natural product has been already observed by BAUP\*; and it is probable that many other of the resins which exude from trees belonging to the pine and its kindred tribes, contain, in like manner, a crystallizable resin possessed of a peculiar elementary constitution. These two classes of resins have hitherto been distinguished only by the general names of pinic and sylvic acids, though the several members of each class are at least as different in composition as the two resins themselves, which have been regarded as the types of each class.

This observation, suggested by the examination of the natural resin of the *Pinus Abies*, is confirmed by an analysis of  $H_{ESS} \not\uparrow$ , of a crystalline resin which he obtained as sylvic acid, but which he found to be composed of  $C_{40}$   $H_{30}$   $O_8$ , and for which, though he is unacquainted with the natural resin from which it was extracted, he has proposed the name of *Oxysilvic*. This name it is obvious would apply to the crystalline resin of the *Pinus abies*; it is therefore desirable that some other more general nomenclature for this class of bodies should be devised.

The quantity of the crystallizable resin which they contain varies in different portions of the natural product. Such is the case with elemi resin, of which some specimens dissolve completely in cold alcohol; such is the case with colophony; and such also is the case with the resin above analysed. In examining a mass of the natural resin, parts of it will be found to be harder than the rest, whiter, having a lamellar fracture, being tough and yet friable; in these portions the crystallizable con-

<sup>\*</sup> Annales de Chimie et de Physique, tom. xxxi. p. 108. He calls it abietic acid, and describes it as an acid resin soluble in 7.5 of common alcohol (88 per cent.) at 57° FAHR., and crystallizing in quadrangular plates.

<sup>†</sup> Poggendorf's Annalen, tom. xlvi. p. 326.

stituent exists in greatest quantity. If the action of the air have any influence in changing the chemical constitution of the natural turpentines as they exude from the trees, it is not difficult to understand either how one portion should combine with five and another with six of oxygen, or how the quantity of each of these compounds present in any two masses should be found to be very different.

The solutions of both the resins of *Pinus abies* in alcohol gave precipitates with an alcoholic solution of acetate of lead, but I have not examined any of their salts.

## VIII. Resin of Olibanum, the Frankincense of the Ancients.

When the olibanum of the shops, consisting of rounded masses, differing to the unpractised eye only in depth of colour, was introduced into alcohol, some pieces were rendered clear and transparent, while others became almost immediately white and opake, from a white powdery coating left on their surface as the soluble portion is taken up by the fluid. That the mixture of these two varieties had not been made recently, appeared from the manner in which pieces of the different kinds cohered and were occasionally imbedded in each other, as if the contact had taken place while they were comparatively soft.

I. Before I perceived this difference a considerable portion was already dissolved. I therefore filtered the solution, and evaporated a portion of it in a thin film. The two varieties also were separated from each other, and covered each with fresh alcohol.

Of the resin obtained by evaporating the solution of the mixed varieties,

11.236 grains gave 
$$\ddot{C} = 30.72$$
,  $\dot{H} = 10.40$ , or per cent.,  
Carbon =  $75.59 = 40$  atoms.  
Hydrogen =  $10.28 = 32.2$  atoms.  
Oxygen =  $14.13 = 5.71$  atoms.

II. The lumps which had retained their transparency when first digested in cold alcohol, were acted on more slowly by this menstruum than the other variety. They however after a time became covered with an opake white coating, but it was less in quantity than the similar insoluble matter left by the other. The pale-yellow solution was evaporated in a thin film, and kept for sixty hours at a temperature of 200° FAHR. The resin was pale-yellow, brittle, and cracked on cooling, and became soft at 220° FAHR.

A. 13·1 grains gave 
$$\ddot{C} = 37.58$$
, and  $\dot{H} = 12.69$ .

B. Another portion of the same solution evaporated and heated for eighteen hours, gave a resin of which 10·17 grains gave  $\ddot{C} = 29\cdot047$ , and  $\dot{H} = 9\cdot767$ .

9.695 grains gave 
$$\ddot{C} = 27.73$$
, and  $\dot{H} = 9.376$ .

These are equal to

These results agree very nearly with the formula  $C_{40}$   $H_{32}$   $O_4$ , being that originally adopted by Rose to represent the constitution of colophony. This formula gives

40 Carbon = 
$$3057.480 = 79.27$$
  
32 Hydrogen =  $399.347 = 10.36$   
4 Oxygen =  $400.000 = 10.37$   
 $3856.827$  100

The most marked disagreement is in the amount of hydrogen which by analysis is about one tenth per cent. greater than it should be, allowing for the usual errors of analysis. The formula  $C_{40}$   $H_{33}$   $O_4$  would give 10.6 per cent. of hydrogen, which is probably too near the quantity found to represent the amount actually present in the resin.

At the same time I would take the present opportunity of repeating\*, that in none of the formulæ deduced from the analyses detailed in the present investigation, is the number of equivalents of hydrogen to be considered as absolutely determined. Whatever precautions may be taken to obtain any given resin in a normal or perfectly pure state, and to avoid the ordinary errors of experiment, the examination of every new member of this interesting family convinces me that though the formula deduced from analysis may express very truly the relations between the number of the equivalents of carbon and oxygen, yet that the hydrogen is doubtful to the extent of one or two equivalents always in excess, and that to this extent, therefore, the formula I have given may be still open to correction.

- III.—1. Of that which became soonest opake from containing the largest quantity of gum, two several portions of the solution were evaporated in thin films, and heated for sixteen hours at 250° Fahr.
  - A. Of the first portion 10.22 grs. gave  $\ddot{C} = 28.67$ , and  $\dot{H} = 9.575$  grs.
  - B. Of the second portion 6.33 grs. gave  $\ddot{C}=17.693$ , and  $\dot{H}=5.908$  grs.

These are equal to

Carbon = 
$$77.57 = 77.29$$
  
Hydrogen =  $10.41 = 10.37$   
Oxygen =  $12.02 = 12.34$   
 $100$   $100$ 

<sup>\*</sup> Ante, p. 286.

The formula  $C_{40}$   $H_{32}$   $O_5$  gives

Carbon = 
$$77.28$$
  
Hydrogen =  $10.09$   
Oxygen =  $12.63$   
 $100$ 

2. Exhausted with more alcohol, this portion gave a resin of a different constitution, which did not harden so readily on cooling even after long heating, and was obtained brittle only in very thin films.

C. 10·435 grs. gave 
$$\ddot{C} = 28\cdot39$$
, and  $\dot{H} = 9\cdot35$ .  
D. 5·67 grs. gave  $\ddot{C} = 14\cdot49$ , and  $\dot{H} = 4\cdot867$  or

$$\begin{array}{cccc}
C. & (7.) & D. & (8.) \\
75\cdot23 & = & 74\cdot66 \\
Hydrogen & = & 9\cdot95 & = & 10\cdot07 \\
Oxygen & = & 14\cdot82 & = & 15\cdot27 \\
\hline
100 & 100
\end{array}$$

The formula  $C_{40}$   $H_{32}$   $O_6$  requires

Carbon = 
$$75.36$$
  
Hydrogen =  $9.84$   
Oxygen =  $14.80$   
 $100$ 

These discordant results seemed to imply that this gum resin contains two resins, of which the one is represented by  $C_{40}$   $H_{32}$   $O_4$ , and the other by  $C_{40}$   $H_{32}$   $O_6$ . This would account for the formula  $C_{40}$   $H_{32}$   $O_5$  given by the above analyses A. and B., on the supposition that the resin employed in these analyses was a mixture of the two, as well as for the occurrence of the resin with four equivalents, *alone*, in some varieties of olibanum.

3. With the view of satisfactorily determining this point, a further quantity of olibanum was immersed in alcohol, and the portions which soonest exhibited a coating of gum were selected. Treated with cold alcohol for several days with occasional agitation, these gave a pale yellow solution which was decanted. The undissolved part was boiled with more alcohol, and a much paler solution obtained. This paler solution evaporated in a thin film, as usual, gave a brittle resin, having the colour and much of the smell of colophony, of which

E. 7.20 grs. gave 
$$\ddot{C} = 19.51$$
, and  $\dot{H} = 6.43$  or per cent.

Carbon =  $74.93$ 
Hydrogen =  $9.92$ 
Oxygen =  $15.15$ 

which agrees with the results C. and D., and leaves no doubt that a resin with six atoms of oxygen is one of those which exist in olibanum. The first, or yellower solution, gave a softer resin, the analysis of which was lost by a failure in the burning.

4. On examining the olibanum of commerce after the above experience of the presence of different resins, it is easy to distinguish by the eye at least two varieties; one in rounded brittle, brownish-grey, opaque masses of various sizes; the other in long tears as if it had flowed more easily from the tree, and been less rounded by attrition, often softer, less brittle, and less dull in aspect. There occur also other pieces not to be classed with either, the composition of which can be determined only by a separate examination\*. The first variety described is that which contains most gum.

A few pieces of this were carefully selected and treated with alcohol for several days in the cold till the resin was entirely exhausted. The whole of the solution was evaporated together, and the resin heated at 250° Fahr. for sixteen hours.

8.03 grs. gave 
$$C = 21.87$$
, and  $H = 7.215$  or

Carbon =  $75.31$ 

Carbon =  $9.98$ 

Oxygen =  $14.71$ 
 $100$ 
 $100$ 
 $100$ 

These selected portions, therefore, consisted wholly of gum in large quantity, and of a resin containing six of oxygen; and as we have already seen that those pieces which include less gum, consist wholly of gum and a resin containing only four of oxygen, and having much of the smell and other properties of colophony, I have thought it unnecessary to search for any other explanation of the discordant results exhibited in analyses 5 and 6, than the supposition that the resin employed in these analyses was a mixture of the two. Had I chosen to omit these two analyses from the present paper, no discordance would have appeared among the results detailed. I think it better, however, that in an investigation like the present, no important steps should be omitted, both because they illustrate the precautions it is necessary to adopt in order to obtain a pure substance, and because others who may repeat my experiments, should they obtain repeated results agreeing so closely, and indicating so distinct a formula as the analyses 5 and 6 (above), might consider themselves justified, without further examination, in pronouncing me to have been in error.

Conclusions.—The gum resin olibanum of commerce consists of a mixture of at least two gum resins, the resinous ingredient in each of which differs from that of the other in composition and properties.

<sup>1.</sup> The rounded, opaque, dull, hard, and brittle pieces, which speedily become covered

<sup>\*</sup> These remarks I believe to apply generally to the olibanum as it is met with in this country, the first quantity I examined being bought in Edinburgh six years ago, the second in London within these few months.

with a white crust when immersed in alcohol, contain an acid resin (A.) =  $C_{40}$   $H_{32}$   $O_6$ . This variety constitutes the larger portion of the olibanum of commerce, and is the more fragrant when burned. Its composition is determined by the four concordant results (7, 8, 9, 10). It contains a variable quantity of a volatile oil, as is the case with nearly all the resins, by which some specimens even after long heating are prevented from immediately becoming brittle when allowed to cool.

2. The clearer, yellower, less brittle and opaque pieces, generally in long tears (stalactitic?) as they have flowed from the tree, and which give less gum when treated with alcohol, contain a resin represented by  $C_{40}$   $H_{32}$   $O_4$ , and having considerable resemblance in smell and in its other properties to colophony.

Whether these two varieties issue from different parts of the same tree, or at different seasons, or whether the true olibanum is mixed with the produce of another tree, it is not easy to determine. We can scarcely believe that the two varieties issue from the same tree under the same circumstances.

As I have already said, there may be other resins mixed with these in smaller quantity, in the olibanum of commerce, in regard to the composition of which I have made no examination.

## General Observations.

We have already seen in the first and second parts of this inquiry, that the resins may differ very widely in the number of equivalents, not only of oxygen, but also of hydrogen, which they contain; and founding on this difference in respect of the hydrogen, we have seen reason also to divide such as have hitherto been analysed into two groups, represented respectively by the general formulæ

$$C_{40} \ H_{32-x} \ O_y$$
 and  $C_{40} \ H_{24-x} \ O_y$ .

The resins described in the present paper belong to the first of these groups, and illustrate very clearly the differences which may exist in the number of equivalents of hydrogen among the several members of the same group. A comparative inspection of the formulæ is sufficient to satisfy us that such differences exist in nature.

Resin of *Pinus abies* B =  $C_{40}$  H<sub>29</sub> O<sub>5</sub> Resin of Sandarach A =  $C_{40}$  H<sub>31</sub> O<sub>5</sub> Resin of *Pinus abies* A =  $C_{40}$  H<sub>29</sub> O<sub>6</sub> Resin of Sandarach C =  $C_{40}$  H<sub>30</sub> O<sub>6</sub> Resin of Sandarach B =  $C_{40}$  H<sub>31</sub> O<sub>6</sub> Resin of Olibanum A =  $C_{40}$  H<sub>32</sub> O<sub>6</sub>.

At present I do not dwell on these partial generalizations, as the results of other experiments which I shall hereafter have occasion to detail will render necessary a slight modification of one or both of the above general formulæ.

Durham, May, 1839.