

IX. *On the Constitution of the Resins.* By JAMES F. W. JOHNSTON, Esq. M.A. F.R.S.,  
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THE object of the investigation, of which the present paper forms a part, is

1. To determine the relative composition of the various resins which occur in nature. Possessing so many properties in common, this large family of natural productions ought also to present many analogies in constitution.

2. To ascertain how far they may be considered as derivatives from one common radical; and

3. Whether it is possible to represent them all by one or more general formulæ.

I. *Resin of Mastic.*

Mastic resin is said to be obtained from the *Pistacea lentiscus*, and to be produced chiefly in the island of Chios. It occurs in drops or tears, which are transparent, and of a pale yellow colour. It melts at  $212^{\circ}$ , and emits a peculiar and not unpleasant odour. Fused in a retort it gives off an acid liquid in small quantity. If the heat be raised to  $300^{\circ}$  FAHR. and upwards, the melted mass froths up, and water and acid vapours are evolved. At a higher temperature a pale yellow liquid distils over very slowly, at first of the consistence of oil, but increasing in thickness as the process proceeds, water and acid being also given off during the whole process. What remains in the retort is of a black colour, and nearly insoluble in alcohol.

Digested in cold alcohol, mastic resin is in great part dissolved; what remains is nearly pure white, elastic, capable of being drawn out into long fibres of a silky lustre, and is a compound with alcohol of a second resin (B), very sparingly soluble in alcohol, but more largely in an alcoholic solution of resin A. Hence the solution obtained contains a portion of the second resin, which may be in a great measure precipitated by large dilution with alcohol.

I. The solution of resin A thus obtained is of a pale yellow colour. Distilled and evaporated at  $212^{\circ}$  FAHR., it gives a pale yellow resin flowing freely at that temperature, but at higher temperatures frothing up and giving off alcohol.

Of a portion fused at  $350^{\circ}$  FAHR. till it ceased to emit bubbles of vapour,

8.67 grains gave  $\ddot{C} = 24.685$ , and  $\dot{H} = 8.18$   
 10.73 grains gave  $\ddot{C} = 30.335$ , and  $\dot{H} = 9.80$   
 10.294 grains gave  $\ddot{C} = 29.16$ , and  $\dot{H} = 9.614$

These results give per cent.

	(1.)	(2.)	(3.)
Carbon	= 78·729	78·172	78·328
Hydrogen	= 10·483	10·337	10·377
Oxygen	= 10·788	11·491	11·295
	100	100	100

These agree nearly with the formula  $C_{40} H_{32} O_4$ , which gives

Carbon	= 79·275
Hydrogen	= 10·355
Oxygen	= 10·370
	100

and was adopted by ROSE as representing the constitution of colophony. The carbon, however, is deficient, and the hydrogen, according to the more recent analyses of TROMMSDORF, LIEBIG, and LAURENT, is in larger quantity than in either the pinic or sylvic acid. I therefore dissolved in alcohol a second portion of the mastic of the shops, diluted the solution largely\* with alcohol to separate the resin B, evaporated and heated to 260° FAHR. for eighteen hours, stirring it occasionally as long as bubbles of vapour were evolved in any quantity.

Of this resin 10·38 grains gave  $\dot{C} = 29·785$ , and  $\dot{H} = 9·48$ , or

	(4.)
Carbon	= 79·343
Hydrogen	= 10·147
Oxygen	= 10·510
	100

which is almost identical with the result of ROSE for the crystallized resin of copaiva balsam.

II. Heated again in the air to 350° FAHR. it had lost its fragrant odour, and emitted white vapours. In this state 8·718 grains gave  $\dot{C} = 25·16$  and  $\dot{H} = 8·02$  grains. These are equivalent to

	(5.)	$C_{40} H_{30} O_4$ gives
Carbon	= 79·800	79·79
Hydrogen	= 10·221	9·77
Oxygen	= 9·979	10·44
	100·000	100·000

The carbon in this analysis is the exact theoretical quantity required by LIEBIG'S formula for the sylvic and pinic acids, but the hydrogen is still considerably in excess.

\* The solution from which the resin first analysed was obtained had not been diluted, as I was not then aware that by this means resin B would be more effectually separated. The resin A of analysis 1, 2, 3, might therefore contain a portion of resin B.

The resin thus analysed, however (5.), had undergone a change of constitution by being heated to 330°, for, when treated with alcohol, a large portion of it refused to dissolve, remaining behind as a soft reddish resin, on which the alcohol of the shops appeared to have little action in the cold.

After taking up all that was soluble, the alcoholic solution was evaporated, and the resin heated for two hours to 260° FAHR. It was transparent, reddish yellow, and very beautiful. On analysis 10·965 grains gave  $\ddot{C} = 31\cdot925$   $\dot{H} = 10\cdot742$  grains, which are equal to

$$\begin{array}{r} \text{Carbon} = 80\cdot507 = 40 \text{ atoms} \\ \text{Hydrogen} = 10\cdot885 = 33\cdot11 \text{ atoms} \\ \text{Oxygen} = 8\cdot608 = 3\cdot27 \text{ atoms} \\ \hline 100 \end{array}$$

The soluble part therefore of the changed resin was no longer pure mastic resin A (see *infra* analysis, Nos. 26, 27, 28.).

III. A third portion of the mastic of the shops was boiled in water for several hours, by which it was rendered white, opaque, and less fusible, probably from the loss of a portion of volatile oil existing in the resin of commerce. It was then digested in a large quantity of alcohol, in which it now also dissolved more slowly. The solution was evaporated, and the resin obtained again boiled in water for a length of time to drive off the whole of the alcohol.

1. A portion of this resin was then heated to about 240° FAHR., when it fused freely and ran smooth, and when cold had the same beautiful colour and appearance as that previously analysed.

10·956 grains gave  $\ddot{C} = 31\cdot35$ , and  $\dot{H} = 10\cdot136$ , or per cent.

$$\begin{array}{r} \text{Carbon} = 79\cdot122 \\ \text{Hydrogen} = 10\cdot279 \\ \text{Oxygen} = 10\cdot599 \\ \hline 100 \end{array}$$

2. A second portion was heated only to 212° for 48 hours, when it had become transparent and of a pale yellow colour. At this temperature it softened, but did not enter into perfect fusion. It still showed a tendency to form minute bubbles of gaseous matter.

10·713 grains gave  $\ddot{C} = 30\cdot71$ , and  $\dot{H} = 10\cdot02$  grains, or per cent.

$$\begin{array}{r} \text{Carbon} = 79\cdot265 \\ \text{Hydrogen} = 10\cdot392 \\ \text{Oxygen} = 10\cdot343 \\ \hline 100 \end{array}$$

The resin employed in these last analyses (7. and 8.) was entirely dissolved when treated with alcohol, No. 7. leaving only a trace of insoluble matter. They may be considered therefore as representing very nearly the constitution of the soluble resin of mastic. The formula  $C_{40} H_{31} O_4$  agrees very closely with these results, and with that of analysis No. 4, thus :

	Calculated.	(7.) Exper.	(8.) Exper.	(4.) Exper.
40 Carbon = 3057·480	= 79·531	79·122	79·265	79·343
31 Hydrogen = 386·867	= 10·063	10·279	10·392	10·147
4 Oxygen = 400·000	= 10·406	10·599	10·343	10·510
	3844·347	100	100	100

If this be the true composition, it shows a close approximation to the pinic and sylvic acids, and yet a cause for the difference in the sensible properties exhibited by these different kinds of resin. If such differences should actually be found to exist in nature, the striking fact will at once suggest itself, that under the general expression  $C_{40} H_{32-x} O_4$  we may have a great variety of resins; and a still greater variety, exhibiting also more sensible differences in their physical properties under the more general one of  $C_{40} H_{32-x} O_{4+y}$ .

IV. *Action of Heat.*—We have seen that when resin A is heated to  $260^{\circ}$  FAHR. or upwards, it is partly decomposed, and an insoluble portion remains when it is treated largely with common alcohol in the cold. This resin is in mass of a reddish colour, and is soluble in boiling alcohol, from which it falls as a yellow powder on cooling. Dried at  $212^{\circ}$  FAHR. it does not melt, but at about  $130^{\circ}$  it begins to cohere into a dark reddish brown mass. Heated for twelve hours at  $212^{\circ}$ , and afterward exposed to a temperature at which it began to cohere,

A. 8·538 grains gave  $\ddot{C} = 24\cdot33$  and  $\dot{H} = 7\cdot776$

B. 10·994 grains gave  $\ddot{C} = 31\cdot245$  and  $\dot{H} = 9\cdot976$

These are equivalent to

	A. (9.)	B. (10.)
Carbon =	78·762 =	78·943
Hydrogen =	10·119 =	10·128
Oxygen =	11·119 =	10·929
	100	100

2. As these results do not give any clear idea of what takes place when the resin is thus heated, I introduced a portion of the pure resin into a glass retort and kept it fused in a sand bath for twenty-four hours, the heat during the last twelve hours being raised to  $270^{\circ}$  FAHR. Water was deposited in the neck of the retort, rendered sour by a crystallizable acid in small quantity. The heat was withdrawn, when a

pale yellow liquid began to show itself in the upper part of the retort. The resin was red and exceedingly beautiful, and when treated with alcohol was now separable into three portions.

A. Boiled with alcohol of the shops, a portion of a red colour was left, on which this liquid appeared to have little further action. It adhered strongly to the retort, but was separated by boiling water, and obtained in the form of a dirty yellow powder, which, at  $270^{\circ}$  FAHR., showed no symptoms of fusion. Dried at this temperature

8.475 grains gave  $\ddot{C} = 23.625$  and  $\dot{H} = 9.859$ , or

	(11.)	$C_{40}H_{30}O_5$ gives	$C_{40}H_{31}O_5$ gives
Carbon	= 77.080	77.76	77.51
Hydrogen	= 9.859	9.52	9.80
Oxygen	= 13.061	12.72	12.69
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	100	100	100

From a single analysis, which was all that the quantity at my disposal enabled me to perform, it is impossible to determine which of the formulæ represented in columns 2 and 3 is the true one. Probability, however, is in favour of the first, or  $C_{40}H_{30}O_5$ , which indicates that when decomposed by a moderate heat one of the changes which mastic resin A. undergoes is the substitution in a part of it, of an atom of oxygen for one of hydrogen, the new compound being nearly insoluble in common alcohol even at a boiling temperature.

B. The boiling alcoholic solution deposited on cooling a pale yellow resin, which heated and fused, became brownish red.

11.817 grains gave  $\ddot{C} = 33.858$ , and  $\dot{H} = 10.356$  grains.

C. The cold alcoholic solution, when evaporated and heated gently till perfectly transparent, gave a beautiful reddish yellow resin, of which

12.05 grains gave  $\ddot{C} = 34.003$ , and  $\dot{H} = 11.227$  grains.

These results are equal to

	B. (12.)	C. (13.)
Carbon	= 79.225	= 78.026
Hydrogen	= 9.737	= 10.352
Oxygen	= 11.038	= 11.622
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	100	100

From these analyses we cannot derive much information with regard to the constitution of these soluble portions of the changed resin, and it would be necessary to carry the process further than was done in this experiment, before the action of heat can be accurately understood. If we might be guided in our opinions as to the ultimate nature of the soluble part by the constitution of the small quantity of which

No. 6. exhibits the analysis, we should infer that two new resins are produced, in the formulæ for which are found  $O_5$  and  $O_3$  respectively. But the subject requires further investigation, and I hope to be able to return to it at a future period.

V. *Atomic weight of Resin A.* It has been already observed by UNVERDORBEN that the resin of mastic bears a considerable resemblance to colophony, and combines with nearly the same proportion of oxide of lead.

A. *Salts of Lead.* When a solution of this resin in alcohol is mixed with an alcoholic solution of acetate of lead, a white precipitate falls, which, when dried at  $212^\circ$  becomes yellow; at  $350^\circ$  FAHR. it melts into a brownish yellow mass without decomposition.

1. Dried at  $300^\circ$  FAHR. 11.610 grains left 2.307 grains of oxide of lead = 19.878 per cent.

2. Of the same fused at  $350^\circ$  FAHR., 10.33 grains left 2.07 grains of oxide = 20.038 per cent.

These give for the constitution of the salt

	1.	2.	
Resin . . .	80.122	79.962	} . . . . (14.)
Oxide of lead .	19.878	20.038	
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>	
	100	100	

It is therefore a *sesquisalt* =  $1\frac{1}{2} (C_{40} H_{31} O_4) + Pb O$ , which consists of

$$\left. \begin{array}{l} \text{Resin} = 80.527 \\ \text{Oxide} = 19.473 \end{array} \right\} = 100$$

When boiled in alcohol, after being dried at  $300^\circ$  FAHR., this salt is not wholly dissolved. Of that which was left undissolved in one experiment,

	12.17 grains left 3.09 oxide of lead = 25.31 per cent.	} . . (15.)
	8.805 grains left 2.20 oxide of lead = 24.99 per cent.	
in another experiment	8.57 grains left 2.232 oxide of lead = 26.04 per cent.	
	11.491 grains left 3.026 oxide of lead = 26.33 per cent.	

These results agree with the formula  $(C_{40} H_{31} O_4) + Pb O$ , which gives

$$\left. \begin{array}{l} \text{Resin} = 73.388 \\ \text{Oxide} = 26.612 \end{array} \right\} = 100$$

The boiling alcoholic solution deposits on cooling a white precipitate. After being dried at  $300^\circ$ , the portions of this precipitate obtained from the above two experiments were burned in the air.

A. 5.21 grains left 0.994 oxide of lead = 19.079 per cent.	} . . (16.)
5.52 grains left 1.044 oxide of lead = 18.913 per cent.	
B. 9.217 grains left 1.683 oxide of lead = 18.249 per cent.	

The salt thus precipitated is therefore the same as that obtained by the direct ac-

tion of the solutions of resin A. and of acetate of lead on each other. When boiled on this sesquisalt, therefore, the alcohol decomposes it, dissolving a *bisalt* and leaving a *neutral* salt insoluble, while from the solution of the former a *sesquisalt* precipitates on cooling. This accounts for a slight deficiency in the oxide of lead found in these salts; the presence of a small quantity of a more acid salt in each causing a higher percentage of resin than is given by calculation.

When to the acid solution containing acetate of lead and resin A. from which this *sesquisalt* has been separated by filtration, pure ammonia is cautiously added with repeated agitation; a further white precipitate falls, which is *probably* the neutral salt above described. I did not dry this salt, but transferred it whilst still moist into boiling alcohol. After repeated digestion a comparatively small portion only was dissolved, the boiling solution depositing the *sesquisalt* as it cooled. The insoluble salt was collected and dried at 300° FAHR.

5.93 grains left 2.452 of oxide of lead = 41.357 per cent.

It is therefore a *disalt* =  $(C_{40} H_{31} O_4) + 2 Pb O$ , which consists of

By experiment.	Calculated.	
Resin = 58.643	57.96	} . . . . (17.)
Oxide = 41.357	42.04	
<hr style="width: 50%; margin: 0 auto;"/> 100	<hr style="width: 50%; margin: 0 auto;"/> 100	

It appears, therefore, that resin A. of mastic forms with oxide of lead at least four compounds.

*a.*  $2 (C_{40} H_{31} O_4) + Pb O$  obtained in solution on boiling *b* in alcohol.

*b.*  $3 (C_{40} H_{31} O_4) + 2 Pb O$  by mixing the alcoholic solutions of the resin and of acetate of lead, and by subsidence from boiling solutions of *a*.

*c.*  $(C_{40} H_{31} O_4) + Pb O$  left insoluble when *b* is boiled in alcohol.

*d.*  $(C_{40} H_{31} O_4) + 2 Pb O$  left insoluble when the fresh precipitate from ammoniacal solutions of the resin and of acetate of lead is boiled in alcohol.

The compound *a*, as will appear from the preceding detail, is hypothetical, but its existence is necessary to explain the action of alcohol on the *sesquisalt*, and is rendered almost certain by the existence of an analogous silver salt\*.

**B. Salts of Silver.** When an *ammoniacal* solution of nitrate of silver in alcohol is poured into an alcoholic solution of mastic resin A, a pure white precipitate falls, soluble in large excess of ammonia, and becoming reddish brown in the sun's rays. Collected on the filter, and afterwards boiled with alcohol, it is nearly all dissolved, giving a slightly coloured solution, from which on cooling, a bulky white precipitate

\* If from the solution of the *bisalt* a *sesquisalt* precipitate spontaneously, a more acid salt still must remain in solution. Three equivalents of a *bisalt* would allow two of a *sesquisalt* to fall, while one of a *tersalt* would remain in solution. I shall have occasion hereafter to mention other circumstances which render probable the existence of resinous salts which contain three equivalents of acid, and others which contain three of base.

again falls. This bulky precipitate was dried by pressure between folds of bibulous paper, and afterwards at a temperature of  $250^{\circ}$  FAHR.

Dried at  $250^{\circ}$ , and still in the state of a white powder, it left 15.788 per cent. of metallic silver when burned in the air.

At  $300^{\circ}$ , when it cohered, became of a dark colour, and gave a brownish red powder; it left 16.042 per cent. of silver. At  $350^{\circ}$  FAHR. when it began to fuse it left 15.844 per cent.

The mean of these three results is 15.891 per cent. of silver, or 17.066 of oxide of silver, therefore the salt consists of

$$\left. \begin{array}{l} \text{Resin} \quad . \quad . \quad . = 82.934 \\ \text{Oxide of silver} = 17.066 \end{array} \right\} \dots \dots \dots (18.)$$


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100

A compound represented by the formula  $2(C_{40}H_{31}O_4) + AgO$  should contain 15.88 per cent. of oxide of silver, from which it would appear that the above is a bisalt with a small excess of silver. That there are other salts of silver containing less acid is rendered probable by the difficulty of obtaining this bisalt without excess of base.

VI. *Constitution of the Resin Salts.*—There remains still one important question to be solved in regard to the constitution of the salts of this and the other resins. Does the resin unite with the oxide as a whole and without change, as muriatic acid unites with ammonia to form sal-ammoniac, or is it altered in any way, as the organic acids generally are when they combine with bases? Does it part with any of the oxygen or hydrogen it contains, when it forms a metallic salt? This inquiry is a very interesting one, and it is not at all answered by the experiments above detailed. The results obtained are sufficiently wide of the quantities indicated by theory, to admit of considerable changes in the constitution of the resin, the existence of which can only be discovered by the ultimate analysis of the several compounds. In the paper of RosÉ on the constitution of colophony and some of the other resins\*, the relative quantities of acids and base in several of the salts is investigated, but no ultimate analysis of them is given. He only says, that, by the ultimate analysis of the salts, he obtained nearly the same composition for the resin as by analysing the pure resin itself. From this it is fair to infer, that he found a slight difference, which he would naturally attribute to some impurity or imperfection in the salt employed, and would not, therefore, consider these results to be deserving of equal confidence with those obtained from the pure resin. In the actual state of our knowledge in regard to the theory of the saline compounds of organic substances possessing acid properties, it would be a great step in advance were the constitution of the resinous salts accurately made out, and it might be expected to throw much light on the relative constitution of the different resins themselves.

\* POGGENDORFF'S Annalen, xxxiii. p. 32.



1. Of the neutral salt of lead above described, 11.9 grains gave  $\ddot{C} = 25.14$ , and  $\dot{H} = 7.372$  grains. This is equal to

	(19.)	Pb O + (C <sub>40</sub> H <sub>31</sub> O <sub>4</sub> ) gives
Carbon . . =	58.416	58.361
Hydrogen . =	7.372	7.384
Oxygen . . =	7.882	7.643
Oxide of lead =	26.333	26.612
	100	100

2. Of the sesquisalt of lead 2 Pb O + 3 (C<sub>40</sub> H<sub>31</sub> O<sub>4</sub>) 11.28 grains gave  $\ddot{C} = 26.732$ , and  $\dot{H} = 8.446$  grains. This is equal to

	Experiment.	Calculated.	
Carbon . . =	65.529	64.044	}
Hydrogen . =	8.446	8.103	
Oxygen . . =	7.776	8.379	
Oxide of lead =	18.249	19.477	
	100	100	(20.)

The first of these results is very near the theoretical constitution, and could it be *exclusively* depended upon, would indicate C<sub>40</sub> H<sub>30</sub> O<sub>4</sub> as the formula for the resin. The second analysis exhibits an excess of carbon, but the salt was not pure, as the quantity of lead it contained indicates. Want of material prevented me from repeating the analysis. Both results, however, are equally satisfactory in showing, that, in combining with the oxide of lead, the resin parts with none of its oxygen, and that the base does not replace any of the elements which it contains in an uncombined state.

3. Of the *subsalt* 2 Pb O + (C<sub>40</sub> H<sub>31</sub> O<sub>4</sub>) dried at 300° FAHR.

A. 13.6 grains gave  $\ddot{C} = 22.54$ , and  $\dot{H} = 7.064$

B. 14.11 grains gave  $\ddot{C} = 24.00$ , and  $\dot{H} = 7.127$

C. 8.925 grains gave  $\ddot{C} = 14.77$ , and  $\dot{H} = 4.595$ .

These are equal to

	A. (21.)	B. (22.)	C. (23.)
Carbon . . =	45.827	47.033	45.760
Hydrogen . =	5.767	5.612	5.720
Oxide of lead =	41.355	41.355	41.355
Oxygen . . =	7.049	5.998	7.165
	100	100	100

The formula requires

40 Carbon . . =	3057.48 =	46.09
31 Hydrogen . =	386.86 =	5.86
2 Oxide of lead =	2788.99 =	42.04
4 Oxygen . . =	400.00 =	6.01
	6633.34	100

The second analysis B. exhibits a considerable excess of carbon, probably from an error of analysis. All the three, however, agree in representing the hydrogen as less than the formula adopted for the resin requires. A salt consisting of  $(C_{40} H_{30} O_4) + 2 Pb O$  would contain

Carbon . . . =	46·16
Hydrogen . . =	5·65
Oxide of lead =	42·12
Oxygen . . . =	6·07
	100

The quantity of hydrogen is even sufficiently small to allow us to represent the resin by  $(C_{40} H_{29} O_4)$ , while the neutral salt appears to contain  $(C_{40} H_{30} O_4)$ . We can draw no inference in regard to the amount of hydrogen it contains from the analysis of the sesquisalt, from its apparent impurity; but in the other salts of lead the hydrogen present is manifestly less than in the pure resin according to the analyses above given (4, 7 and 8.). Can the metal replace the hydrogen, giving in the one  $C_{40} H_{30} Pb_1 O_5$ , and in the other  $C_{40} H_{29} Pb_2 O_6$ , and can such be the general constitution of the resin salts? This can only be determined by numerous and refined analyses of these compounds.

4. The salt of silver prepared, as already described, by precipitation and subsequent resolution in alcohol, and containing 16·954 per cent. of oxide of silver, gives a different result from those of lead in regard to the constitution of the resin.

A. 12·565 grains after heating to  $300^\circ$  FAHR., when it began to fuse, gave  $\dot{C} = 30\cdot74$ , and  $\dot{H} = 9\cdot704$ .

B. Heated to  $250^\circ$  only, 11·38 grains gave  $\dot{C} = 28\cdot293$ , and  $\dot{H} = 8\cdot9$  grains.

These results give per cent.

	A. (24.)	B. (25.)	Calculated.
Carbon . . . =	67·595	68·673	68·589
Hydrogen . . =	8·581	8·689	8·398
Oxygen . . . =	6·870	5·684	6·732
Oxide of silver =	16·954	16·954	16·281
	100	100	100

The third column is calculated according to the formula  $2 (C_{40} H_{30} O_3) + Ag O$ , and approximates as closely to the experimental results as was to be expected from a salt containing an excess of oxide, probably from the presence in small quantity of a less acid compound.

It appears, therefore, that in uniting with oxide of silver, the elements of an atom of water have been given off, the resin  $C_{40} H_{31} O_4$  becoming  $C_{40} H_{30} O_3 + H O$ . And yet that this is not owing to a simple replacement of hydrogen by silver in the salt, is shown by its containing two equivalents of resin to one of oxide, 2 H O being given off while Ag O only is taken up. It is by no means clearly deducible from these

analyses, therefore, that the constitution of the resin of mastic A. is truly represented by  $C_{40} H_{30} O_3 + H O$ , since during the treatment with silver and ammonia some deeper change may have been effected, giving rise to a new resin represented by  $C_{40} H_{30} O_3$ .

And that this is really the case, seems to be confirmed by an examination of the ammoniacal alcoholic solution from which the salt of silver has been precipitated. When this solution is decanted, and by distillation is concentrated and deprived of its excess of ammonia, it becomes of a brown colour, and a dark brown resin falls to the bottom of the retort or of a jar, into which the solution may be poured. On further concentration, after cooling, more of this resin falls, after which a precipitate of a white silver salt makes its appearance.

Separated by decantation, and kept for twelve hours at  $212^\circ$  FAHR., at which temperature it melted readily,

A. 5.089 grains of this brown resin burned in the open air, left 0.85 of silver, equal to 1.786 per cent. of oxide.

B. 10.97 grains burned with oxide of copper, gave  $\dot{C} = 31.67$ , and  $\dot{H} = 10.565$ .

Correcting B by A, the resin consists of

	(26.)	
Carbon	=	81.280
Hydrogen	=	10.895
Oxygen	=	7.852
		100
		$C_{40} H_{30} O_3$ gives
		81.385
		10.620
		7.995
		100

When dissolved in alcohol a small quantity of a dark brown silver salt was separated. After filtration, evaporation, and fusing at  $212^\circ$  for several hours, the resin was obtained nearly free from silver.

A. 3.061 grains left, when burned in the air,  $0.016 = 0.522$  per cent.

B. 9.158 grains gave  $\ddot{C} = 26.525$ , and  $\ddot{H} = 9.0$ .

C. After heating for several hours at  $300^\circ$  FAHR., during which a fragrant odour was emitted, 10.155 grains gave  $\ddot{C} = 29.40$ , and  $\ddot{H} = 9.933$ .

These gave for the constitution of the resin

	A (27.)	
Carbon	=	80.510
Hydrogen	=	10.976
Oxygen	=	8.514
		100
		B (28.)
		80.474
		10.925
		8.601
		100

If we admit, as is very probable, that the excess of hydrogen and oxygen indicated by these analyses over those obtained in analysis 26. is due to the presence of a small quantity of water, even after heating at  $300^\circ$  FAHR., the three results become entirely accordant\*, and leave little doubt that the constitution of the resin is ex-

\* The discordance in the results thus obtained for the same mass, of the same resin before and after solution

pressed at least very approximately by  $C_{40} H_{32} O_3$ . In looking back upon our previous analyses also, we find in No. 6. a very close agreement with these now given; from which, compared with No. 11., it would appear that by the long continued action of a temperature not below  $350^\circ \text{FAHR.}$  the resin of mastic A, besides other alterations, is changed into a soluble resin containing *three*, and into an insoluble resin containing probably *five* equivalents of oxygen.

The constitution of the resin formed during the preparation of the silver salt, seems thus to confirm the opinion above stated, that a deeper change is produced upon resin A during the treatment with nitrate of silver and ammonia, than the simple extrication of the elements of an atom of water. The large quantity of hydrogen present in the new resin especially supports this view. In the silver salt we have taken  $C_{40} H_{30} O_3$  as the most probable expression for the resin it contains, assuming, as is usually done, that the lowest amount of hydrogen obtained by analysis is greater than the truth. In the analysis of the resin itself the same precautions were taken, yet  $C_{40} H_{32} O_3$  contains the lowest amount of hydrogen which the results permit us to adopt. The presence of moisture in the oxide of copper could not, with the precautions adopted, occasion so great an excess of hydrogen; and in analysis (26.) there is no corresponding excess of oxygen to justify us in attributing the difference to hygro-metric water in the resin itself.

5. With the view of investigating more closely the action of oxide of silver on the resin A, I dissolved a portion of it in alcohol, added to the solution a little caustic ammonia, and afterwards an alcoholic solution of nitrate of silver. The white salt which fell was collected on the filter, washed with cold alcohol, and afterwards dried at  $300^\circ$ . It melts at a low temperature in the alcohol it retains, and is obtained in the form of a dark red porous mass. By a careful regulation of the heat, however, it may be dried without undergoing fusion.

5.177 grains, burned in the air, gave 0.923 of metallic silver = 17.829 per cent.

4.404 grains gave 0.79 = 17.94 per cent. of silver, or 19.26 of oxide of silver.

11.632 grains gave with oxide of copper  $\ddot{C} = 26.87$ , and  $\dot{H} = 8.69$ .

These results give for the composition of the salt

	(29.)	In equivalents.
Carbon	= 63.87	= 40
Hydrogen	= 8.30	= 31.8
Oxygen	= 8.57	= 4.1
Oxide of silver	= 19.26	= 0.6

100

in alcohol, is not without interest in a research into the general constitution of the resins. It shows that, with all our precautions, small differences will occur from circumstances not yet understood, and that in our selection of a formula to represent the constitution of a given resin, we ought to allow *analogy* to influence us in some degree where the results of analysis are not sufficiently numerous and concordant unequivocally to settle the question. To this point I shall have occasion to revert in a future paper on the constitution of certain other resins.

The resin in this salt is evidently  $C_{40}H_{31}O_4$ , or in combining with the silver by this method of preparation it undergoes no change. There is present a considerable excess (one-sixth of the whole) of silver, probably from an admixture of a less acid salt.

After the separation of the salt thrown down as above, nitrate of silver was still added as long as a precipitate fell. This second precipitate was collected and digested in boiling alcohol. A transparent slightly brownish solution was obtained, from which on cooling a white compound fell, but at the same time a considerable portion of a dark brown resin or resinous salt was precipitated on the sides and bottom of the retort in which the solution was effected. The white precipitate was collected and dried at  $300^\circ \text{FAHR}$ .

4.167 grains left 0.64 of metallic silver = 15.36 per cent., or 16.496 of oxide of silver.

A. 11.975 grains, burned with oxide of copper, gave  $\ddot{C} = 28.62$ , and  $\dot{H} = 9.195$ .

B. 8.67 grains gave  $\dot{H} = 6.703$ , the carbonic acid being lost.

The salt therefore consists of

	A. (30.)	B.	$2(C_{40}H_{31}O_4) + AgO$ gives
Carbon	= 66.086		66.79
Hydrogen	= 8.530	8.59	8.46
Oxide of silver	= 16.496		15.88
Oxygen	= 8.888		8.87
	100		100

The bisalt of oxide of silver therefore, prepared without large excess of ammonia, is not decomposed by solution in pure alcohol, the change produced upon it and upon the resin in the former experiment being due either to the excess of ammonia or to the long boiling. Still though the salt obtained in this instance contained the unchanged resin A, yet when the alcoholic solution from which the precipitates were originally thrown down, was concentrated by distillation, there fell, on allowing the solution to cool, first, a portion of a white precipitate, and afterwards, on still further concentration, a quantity of a dark coloured resin, closely resembling the  $C_{40}H_{32}O_3$ , above described and analysed. It appears therefore to be easily reproducible, though the circumstances *necessary* to its production require further investigation.

In regard to the hydrogen contained in this salt, the analysis seems to indicate thirty-one equivalents, which does not agree with the change undergone by the resin in combining with the oxide of lead. It is not impossible, however, that the true formula for the salt may be  $AgO + (C_{40}H_{30}O_4) + (C_{40}H_{31}O_4)$ , which would give 8.34 per cent. of hydrogen, a quantity not differing from 8.53 found by analysis, more than the ordinary results of experiment do from the calculated results; but upon this subject I would not be understood to express a decided opinion until it has undergone further examination\*.

\* In all these analyses the method of LIEBIG has been adopted, with the use of the cork; there seems, however, much weight in the observation of BERZELIUS, that where the number of atoms of hydrogen is great this method may lead to error. While a damp cork may give out, a perfectly dry one may absorb moisture.

VII. *Insoluble Resin of Mastic* (Resin B.). When crude mastic resin is digested in cold alcohol a variable quantity remains undissolved. This portion is soft, tenacious, and elastic like bird-lime, of a silky lustre, and may be boiled in alcohol without sensible diminution. When boiled in water it becomes harder and less elastic; but when deprived of water by drying at  $300^{\circ}$  FAHR., at which temperature it is in a semifused state, it may be drawn out into long fibres, and even when cold it is tough and has some of the elasticity of caoutchouc.

1. Burned in the open air it left a small gray residue of carbonate of lime, being earthy matter mixed with the natural resin.

6.358 grains left  $0.06 = 0.945$  per cent.

2. Burned with oxide of copper after drying at  $300^{\circ}$  FAHR.

A. 12.863 grains gave  $\ddot{C} = 38.624$ , and  $\dot{H} = 12.645$ .

B. 11.605 grains gave  $\ddot{C} = 34.75$ , and  $\dot{H} = 11.395$ .

These results, allowing for the small quantity of foreign matter present (0.954 per cent.), are equivalent to

	(31.)	(32.)
Carbon	= 83.823 =	83.589
Hydrogen	= 11.027 =	11.013
Oxygen	= 5.160 =	5.398
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	100	100

The formula which approaches nearest to these results is  $C_{40} H_{31} O_2$ , giving

40 Carbon	= 3057.480 =	83.613
31 Hydrogen	= 399.347 =	10.920
2 Oxygen	= 200.000 =	5.467
	<hr style="width: 50%; margin: 0 auto;"/>	<hr style="width: 50%; margin: 0 auto;"/>
	3656.827	100

The slight excess of carbon in the first analysis is probably due to some accidental cause. It may have been from a greater admixture of foreign matter in the one portion than in the other, that the small difference has arisen.

When this resin is exposed to a higher temperature it swells, gives off the odour of naphtha (?), and the porous mass, when cold, is no longer soft but brittle. Analysed in this state it gave the formula ( $C_{40} H_{31} O_3$ ), but I did not ascertain how much foreign matter this specimen contained, and the coincidence of the result with this formula may be accidental.

This resin does not sensibly dissolve in a solution of caustic potash, it is, therefore, most probably not an acid resin.

VIII. *Conclusions*.—In regard to the resin of mastic, it therefore appears, from the preceding examination,

1. That it consists of two resins represented respectively by the formulæ (analyses 4, 7, 8, and 31, 32).

The soluble, or resin A. by  $C_{40} H_{31} O_4$  an acid resin.

The insoluble, or resin B. by  $C_{40} H_{31} O_2$  not an acid.

2. That even when considerable care is taken, a series of analyses may be obtained which do not indicate the true constitution of a resin (see analyses 1, 2, 3.).

3. That when exposed to the prolonged action of a temperature exceeding  $300^\circ F_{AHR.}$ , resin A. of mastic, among other changes, seems to be partly altered into a resin containing three, and into one containing five of oxygen,  $C_{40}$  being constant (analyses 6, and 11.). These resins are probably represented by

A =  $C_{40} H_{32} O_3$ , very soluble in alcohol.

B =  $C_{40} H_{30} O_5$ , sparingly soluble in alcohol.

4. That it combines with bases forming four series of salts, which in the case of oxide of lead consist of (see analyses 14, 15, 16, 17.),

1. Two equivalents of resin and one of oxide.

2. Three equivalents of resin and two of oxide.

3. One equivalent of resin and one of oxide.

4. One equivalent of resin and two of oxide.\*

5. That in combining with bases, resin A. does not part with any of its oxygen, but that *if any change take place* in its constitution it is in the hydrogen being replaced by an equivalent proportion of a metal (analyses 19, 21, 22, 23, 24, 25, and 30.). The salts of lead would on this view be represented by

1.  $C_{40} H_{31} O_4 + C_{40} H_{30} Pb_1 O_5$ .

3.  $C_{40} H_{30} Pb_1 O_5$ .

2.  $C_{40} H_{31} O_4 + 2 (C_{40} H_{30} Pb_1 O_5)$ .

4.  $C_{40} H_{29} Pb_2 O_6$ .

I regret to be obliged to leave this interesting part of the subject in an undetermined state, but it will require many often repeated analyses to determine whether this law be generally obeyed by the resins in their combinations with bases.

6. That resin A. by boiling in contact with ammonia and nitrate of silver, or perhaps with nitrate of ammonia †, is changed into a resin, represented, when uncombined, by  $C_{40} H_{32} O_3$ . This resin forms a *bisalt* with oxide of silver, in which there

\* A notation for the resins is very desirable. If the initial letter of the name be adopted, and *r* be put over it to denote resin, and *a*, *b*, be subjoined to distinguish the several resins contained in one natural product, a notation would be obtained easily intelligible, occupying little space, and which would interfere with no other chemical notation yet adopted. Thus the two resins of mastic would be represented by  $\overset{ra}{M}$ ,  $\overset{rb}{M}$ , and the salts of lead formed by resin A. by  $Pb \overset{ra}{M}_2$ ,  $2 Pb + 3 \overset{ra}{M}$ ,  $Pb \overset{ra}{M}$ ,  $2 Pb + \overset{ra}{M}$ .

† Since the above was transmitted to the Royal Society I have tried the effect of boiling resin A. with nitrate of ammonia. Solutions of this salt and of resin A. were mixed and repeatedly distilled, with fresh additions of alcohol. The resin became darker in colour, and much more soluble in boiling than in cold alcohol. After

is also an apparent replacement of hydrogen by silver\*, the resin in this salt (analyses 24 and 25) being represented by  $C_{40} H_{30} O_3$ .

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## II. *Resin of Dragon's Blood.*

Two varieties of dragon's blood are common in this country; one in long stalks or quills inclosed in a leaf, or reed, and presenting the appearance of having been softened by heat previous to being rolled into this form; the other in lumps of considerable size, less compact, and mixed with a large quantity of vegetable and other foreign matter.

1. The purer variety in quills gave, on digestion in alcohol, and evaporation of the solution on the water bath, a resin almost black by reflected light, translucent, in thin fragments, and of a bright red by transmitted light, and in powder of a dark red colour. In preparing these resins it is difficult to determine at what temperature the whole of the alcohol or ether is driven off, and when the frothing up is due to the decomposition or disengagement of volatile matter from the resin itself. This is especially the case in regard to such as, like the present, melt at a low temperature. If the solution in alcohol or ether be evaporated at  $180^{\circ}$  FAHR. till it flows smooth and ceases to change in consistency, it will be found still to froth up and give off vapours having a peculiar, at first agreeable, afterwards *astringent* (?) † odour, if the heat be raised to  $212^{\circ}$ . That a change of composition ensues from a greater increase of temperature appears from the following analyses.

A. A portion of the solution in alcohol was evaporated and heated for a short time at  $212^{\circ}$  FAHR. 11.3 grains gave  $\ddot{C} = 29.43$ , and  $\dot{H} = 6.084$  grains.

B. A second portion was evaporated at  $212^{\circ}$ , and afterwards raised for a few minutes to  $220^{\circ}$  FAHR. 11.16 grains gave  $\ddot{C} = 29.04$ , and  $\dot{H} = 6.135$  grains.

C. The same heated to  $280^{\circ}$  FAHR. frothed up, emitting vapours having an *astringent* alcoholic odour, accompanied with considerable pungency. It was still entirely soluble in alcohol.

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boiling in water and drying at  $300^{\circ}$  FAHR., 10.04 grains gave  $\ddot{C} = 28.89$ , and  $\dot{H} = 9.445$  grains, or per cent.

$$\left. \begin{array}{l} \text{Carbon} = 79.56 \\ \text{Hydrogen} = 10.45 \\ \text{Oxygen} = 9.98 \end{array} \right\} 100.$$

By comparing this result with analyses 4, 7, and 8, it will be seen that the resin had undergone no change in composition, but was still  $C_{40} H_{31} O_4$ .

\* If the resin be  $C_{40} H_{31} O_3$ , then  $(C_{40} H_{31} O_3) + (C_{40} H_{30} O_3) + Ag O$  would agree satisfactorily enough with analyses 24 and 25.

† I venture to use this term, as it, more nearly than any correct one, describes the sensation.



12.42 grains gave  $\ddot{C} = 32.965$ , and  $\dot{H} = 6.94$  grains.

These results are equivalent to

	At 212°.	At 220°.	At 280°.
Carbon	= 72.015	71.887	73.435
Hydrogen	= 5.982	6.108	6.208
Oxygen	= 22.003	22.005	20.357
	<hr style="width: 50%; margin: 0 auto;"/> 100	<hr style="width: 50%; margin: 0 auto;"/> 100	<hr style="width: 50%; margin: 0 auto;"/> 100

Had the results contained in the first and second columns been obtained from the same specimen, we might have concluded that up to 220° FAHR. no sensible decomposition takes place. As however these results, though they approximate to the formula  $C_{40} H_{20} O_9$ , are yet not *accurately* represented by any formula in which the carbon is expressed by  $C_{40}$ , I thought it necessary to analyse the resin prepared by evaporating a solution at a temperature never exceeding 180° FAHR.

2. For this purpose I took the common dragon's blood in lumps, and digested two separate portions in alcohol and ether, and filtered and evaporated the solutions in broad shallow dishes. The resin thus obtained was kept for twelve hours in a stove, the temperature of which was generally considerably under 180° FAHR. At this temperature the resin from the ethereal solution was to the last softer, and contained more air-bubbles than that from the alcohol. Both were of a brilliant red colour, contracted and cracked in every direction on cooling, and in fragments were exceeding electrical.

A. Of that from alcohol 10.25 grains gave  $\ddot{C} = 27.523$ , and  $\dot{H} = 5.95$  grains.

B. Of that from ether 11.65 grains gave  $\ddot{C} = 31.177$ , and  $\dot{H} = 6.987$  grains.

These are equal to

	A.	B.
Carbon	= 74.247	= 73.998
Hydrogen	= 6.450	= 6.663
Oxygen	= 19.303	= 19.339
	<hr style="width: 50%; margin: 0 auto;"/> 100	<hr style="width: 50%; margin: 0 auto;"/> 100

These results agree very nearly with the formula  $C_{40} H_{21} O_8$ , which gives

40 Carbon	= 3057.480 = 74.218
21 Hydrogen	= 262.091 = 6.362
8 Oxygen	= 800.000 = 19.420
	<hr style="width: 50%; margin: 0 auto;"/> 4119.571    100

3. The close accordance of these results with a formula containing eight of oxygen, induced me to return to the *reed* dragon's blood, with the view of ascertaining whether the two varieties were really unlike in constitution, or whether the differences obtained by analysis might not result from the mode in which the resin was extracted,

or the greater or less quantity of the solvent (alcohol or ether) they were permitted to retain. A portion of it therefore was digested in ether, and the solution evaporated.

A. Evaporated and kept for twelve hours at  $150^{\circ}$  FAHR., 12.31 grains gave  $\ddot{C} = 32.606$ , and  $\ddot{H} = 6.757$ .

B. Kept for twelve hours at  $190^{\circ}$  FAHR., 11.12 grains gave  $\ddot{C} = 29.563$ , and  $\ddot{H} = 6.195$ .

C. Of another portion evaporated at  $212^{\circ}$ , and kept at this temperature for six hours, 11.97 grains gave  $\ddot{C} = 31.685$ , and  $\ddot{H} = 6.44$ .

These results are equivalent to

	A.	B.	C.
Carbon	= 73.240	= 73.512	= 73.193
Hydrogen	= 6.099	= 6.190	= 5.978
Oxygen	= 20.661	= 20.298	= 20.829
	<hr style="width: 80%; margin: 0 auto;"/>	<hr style="width: 80%; margin: 0 auto;"/>	<hr style="width: 80%; margin: 0 auto;"/>
	100	100	100

By this prolonged heating of the resin obtained from the pipe or *reed* dragon's blood (as it is called in commerce), by means of ether, it is made to approximate nearer in constitution to the resin from the lump dragon's blood than that which was first analysed. Still there is a deficiency of nearly one per cent. in the carbon, and a considerable deficiency also in the hydrogen, compared with what is required by the formula  $C_{40} H_{21} O_8$  as above given, and which is indicated by the analysis of the lump resin.

What is the cause of the difference, then, and which of the series of analyses is to be considered as representing the true constitution of the pure resin? I place most confidence in the series (2.), for these reasons: *first*, the lump resin is mixed with seeds and fragments of vegetable matter, and is therefore most probably the resin as it exudes from the tree: *second*, the results of the analysis of this variety give an exact formula analogous to those by which so many other resins are represented, and of which the constant  $C_{40}$  is a member; and *third*, the reed dragon's blood, from its porosity, its freedom from foreign substances, and its varying colour (from a bright red to a dirty brown), is evidently a *manufactured* article, the constitution of which therefore is not to be depended upon. Since I have been led to this conclusion, I have learned that a third variety of dragon's blood is brought to the market under the name of *strained*. Now to be strained the natural resin must be made very fluid, and can hardly fail to be more or less decomposed by the temperature necessary to produce the complete fusion. The *reed* variety is probably only the *strained*, made while soft into small rolls and wrapped up.

*Conclusions.*—The following therefore seem to be the conclusions to which the above experiments lead.

1. That the lump dragon's blood is the natural and pure resin, the strained and reed varieties being manufactured articles, and more or less decomposed.

2. That this resin retains alcohol and ether, as most other resins do, with considerable obstinacy, but that these solvents may be entirely expelled by a long-continued (ten or twelve hours) exposure to a temperature not higher than 200° FAHR.

3. That when thus perfectly dried it is represented experimentally by the formula  $C_{40} H_{21} O_8$ .

The two former of these results are of considerable practical importance in an inquiry into the constitution of the resins. Several of those resins which are of the greatest value in a commercial point of view, are said to be subjected to processes of manufacture, by the native collectors, before they are brought into the market; it is therefore of consequence to ascertain that the substance is procured in its unaltered state before it is subjected to analysis. I shall have occasion, in a subsequent part of this inquiry, to mention several resins, the alteration of which by manufacture or adulteration has caused me much loss of time, and, in some cases, prevented me from obtaining a formula on which much reliance is to be placed.

In regard again to the total expulsion of the alcohol or ether, so necessary as solvents of this class of substances, if we evaporate the resins in *mass*, and heat till all the alcohol is driven off, we may often produce decomposition before our purpose is accomplished. It is therefore of great importance to have learned, that long exposure of a thin film of the resin to a low temperature will fully deprive it of those volatile liquids.

*Durham, March 12, 1839.*