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

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IX. *Resin of Scammony.*

When the purest scammony of commerce is digested in cold alcohol, a pale yellow solution is obtained, which, on evaporation, gives a pale yellow, opake, hard, and friable resin. Heated to 300° Fahr. this resin melts, becomes transparent, and emits a peculiar odour. By the action of the alcohol the crude scammony is very little diminished in bulk.

A. After heating forty-eight hours at 250° Fahr. the resin obtained from the alcoholic solution was still in the state of powder, and 12·69 grs. gave $\ddot{C} = 25{\cdot}74$, and $\dot{H} = 9{\cdot}06$ grs.

B. Heated for twelve hours at a temperature at which it cohered, 11·56 grs. gave $\ddot{C} = 23{\cdot}35$, and $\dot{H} = 8{\cdot}162$ grs.

C. Of a third portion fused and kept in a state of quiet fusion for several hours, 11·98 grs. gave $\ddot{C} = 23{\cdot}75$, and $\dot{H} = 8{\cdot}31$.

D. Of a fourth portion fused at 350° Fahr. 9·36 grs. gave $\ddot{C} = 18{\cdot}675$, and $\dot{H} = 6{\cdot}434$ grains.

These results are equivalent to

	A. Heated 48 hours at 250° Fahr.	B. Heated 12 hours at 260° +.	C. Fused for several hours.	D. Fused at 350° Fahr.
Carbon	56·08	55·85	54·82	55·17
Hydrogen	7·93	7·84	7·70	7·63
Oxygen	35·99	36·31	37·48	37·20
	100	100	100	100

I consider the portion B. to represent most nearly the normal state of the resin, and this agrees very closely with the formula $C_{40}\ H_{33}\ O_{20}$, which gives

		Per cent.
40 Carbon	= 3057·500	55·92
33 Hydrogen	= 411·826	7·53
20 Oxygen	= 2000·000	36·55
	5469·326	100

The results C. and D. show that, by further heating, this resin loses both carbon and hydrogen, probably from the disengagement of a volatile substance containing less oxygen than the resin itself. Nearly all the resins when heated to incipient decomposition give off more or less of a volatile oil, but in general the per centage of carbon is increased by such decomposition.

This resin is remarkable for containing the largest quantity of oxygen of any resin hitherto analysed. In this respect it exceeds even the resin of jalap, to which, as the subsequent section shows, it has so much analogy in constitution, and which it resembles also in its action on the system, and in the genus of plants (*convolvolus*) from which it is derived.

X. *Resin of Jalap.*

The resin of jalap is stated by chemical writers, chiefly, I believe, on the authority of CADET DE GASSICOURT[*], to consist of two resins, of which only one is soluble in ether, though both are extracted from the root by alcohol. In this statement, however, there is an error, the source of which will presently appear.

I was induced to turn my attention to this resin in connection with that of Scammony, of which the analysis is above given, in consequence of a statement of GOBEL that this resin contains more oxygen than any other. He found it to consist of carbon 36·62, hydrogen 9·47, and oxygen 53·91[†]. This result, however, is very wide of the truth, and though jalap resin does contain a large per centage of oxygen, it is inferior in this respect to the resin of scammony.

I. The jalap resin of the shops, in lumps of a dark green colour, when digested in ether, gives a dark brown solution, and with the exception of a small quantity of impurities, dissolves entirely. When evaporated, this solution yields a brown resin, emitting, while fused, the distinct and nearly unmixed odour of common colophony. As I had every reason to believe that in this state it is largely adulterated, I did not subject the resin thus obtained to any further examination.

II. An ounce of powdered jalap was digested in alcohol, the brown solution evaporated to dryness, and the dry resinous mass treated with ether. A considerable portion of the mass was taken up by the ether, and alcohol dissolved nearly all that was left. This agrees with the statement of GASSICOURT, who says that of the resin obtained by evaporating the alcoholic solution, ether dissolves $\frac{3}{10}$ths, leaving undissolved a second resin to the amount of $\frac{7}{10}$ths of the entire weight.

III. As the purity of powdered jalap is not to be depended upon, half a pound of the roots was sliced and digested in cold alcohol of the shops, for three weeks, and the solution evaporated. A dark brown mass was obtained, which, after heating to 150° FAHR. for several days, refused to dry up and harden. It presented the appearance, and when warm had the consistence and something of the smell of treacle. It had also a sweetish taste mixed with that of jalap, and when set aside in the cold speedily began to deliquesce.

This mass was treated with boiling water, which dissolved at least two-thirds of

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[*] Handbuch der Chemie, von LEOPOLD GMELIN, ii. p. 569, and THOMSON's Organic Chemistry, p. 540.

[†] Dr. TODD THOMSON's Materia Medica, ii. p. 290, 1833.

the whole, forming a dark brown solution, while the undissolved residue was entirely soluble in ether. The alcoholic extract of jalap, therefore, contains only one resin, which is soluble in ether, two-thirds or upwards of the whole consisting of one or more non-resinous substances soluble in boiling water. It is that portion of these non-resinous substances which ether does not take up, that has hitherto been considered as the second resin of jalap. This explanation reconciles my results with those of Gassicourt, as given in Dr. Thomson's Organic Chemistry; but Leopold Gmelin states not merely that the alcoholic extract, but that this extract *after boiling in water* consists of two resins, one soluble and one insoluble in ether. I am inclined to think, however, that, in transcribing his experiments, Gmelin has written what Gassicourt ought to have done rather than what he did.

The solution of the resin in ether was evaporated and heated at 230° Fahr. till it became dry and solid. It was then reduced to powder and heated for several days to 200° Fahr.

A. 12·75 grs. gave $\ddot{C} = 26{\cdot}19$, and $\dot{H} = 9{\cdot}467$ grs.

Of another portion dried in a thin film,

B. 12·22 grs. gave $\dot{H} = 8{\cdot}973$, the carbonic acid being lost.

C. 10·49 grs. gave $\ddot{C} = 21{\cdot}79$, and $\dot{H} = 8{\cdot}107$ grs.

D. 9·328 grs. gave $\ddot{C} = 19{\cdot}47$, and $\dot{H} = 7{\cdot}056$ grs.

These are equivalent to

	A.	B.	C.	D.
Carbon	56·80		57·44	57·71
Hydrogen	8·24	8·16	8·58	8·40
Oxygen	34·96		34·08	33·89
	100		100	100

I believe that the deficiency of carbon and of hydrogen in the analyses A. and B. is due to the employment of sand of too high a temperature while pumping out the moisture, and that C. and D. represent more nearly the true constitution of the resin. These agree with the formula $C_{40}\ H_{34}\ O_{18}$, which gives

		Per cent.
40 Carbon	= 3057·480	57·88
34 Hydrogen	= 424·306	8·03
18 Oxygen	= 1800·000	34·09
	5281·786	100

This constitution for the resin of jalap being remarkable not merely for the great number of equivalents of oxygen it indicates, but also as presenting the only example we have yet met with (with the exception of the resin of scammony) in which the number of equivalents of hydrogen is decidedly greater than thirty-two, I was anxious to submit it to still further verification: I therefore distilled off the greater portion of the ether from the ethereal solution, and digested the resin a second time in repeated portions of hot water, by which so much was taken up as to give a yellow solution. The water being poured off, the resin was dissolved in alcohol, and a portion of the filtered alcoholic solution evaporated in a thin film, and heated for sixteen hours at 250° Fahr. As before, it had become perfectly dry and brittle, but did not fuse. This resin, however, after evaporation, remains tough for a long time, and does not become friable till after being heated for several hours.

12·36 grs. gave $\ddot{C} = 25·625$, and $\dot{H} = 9·283$, or per cent.,

Carbon	57·34
Hydrogen	8·33
Oxygen	34·34
	100

This result agrees so closely with those previously obtained, that we may consider the presence of thirty-four equivalents of hydrogen in the formula for this resin to be as certainly determined, as we can expect it to be, by the analysis of the uncombined resin, according to our present methods.

XI. *Resin of Labdanum.*

The resin of labdanum is said to be obtained from the *Cystus Creticus,* a native of Syria and of the Grecian Archipelago. It occurs in commerce in the form of black masses, more or less soft and tenacious. Alcohol rarely dissolves more than one-fourth of the whole mass; the solution has a dark-brown colour, a bitter taste, and gives on evaporation a dark-brown transparent resin. This resin has a peculiar, not very unpleasant odour; having, when the resin is hot and melted, a slight resemblance to that of colophony*.

1. A portion of the solution in cold alcohol (0·83) was evaporated at a gentle heat in a thin film, and afterwards heated for six hours to 212° Fahr. When cold the resin was brittle, but the fragments readily cohered when the mass was broken up.

6·635 grs. gave $\ddot{C} = 17·1$, and $\dot{H} = 5·83$ grs.

2. A second portion was evaporated and kept at a temperature of 150° Fahr. for thirty-six hours, and afterwards for four hours at 212° Fahr.

8·115 grs. gave $\ddot{C} = 21·01$, and $\dot{H} = 7·185$ grs.

These results give per cent.,

	1.	2.
Carbon	71·26	71·58
Hydrogen	9·76	9·82
Oxygen	18·98	18·60
	100	100

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* The odour of colophony is that which is generally understood by the term resinous.

The formula $C_{40}\ H_{33}\ O_3$ gives

		Per cent.
40 Carbon	= 3057·440	71·62
33 Hydrogen	= 411·827	9·64
8 Oxygen	= 800·000	18·74
	4269·267	100·

3. The resin in the state in which it had been analysed, as above, was boiled in water, which became slightly coloured, and acquired a bitter taste.

It was then dried by prolonged heating at 212° Fahr., when

5·93 grs. gave $\ddot{C}$ = 15·97, and $\dot{H}$ = 5·34, or per cent.,

	3.	
Carbon	73·99	40 atoms.
Hydrogen	10·00	33·1 atoms.
Oxygen	16·01	7·05 atoms.
	100	

4. This remarkable disagreement with the previous results induced me to boil in repeated portions of water, a second quantity of the labdanum of commerce, and after drying, to digest it in alcohol. The water acquired a brownish colour, and an intensely bitter taste. A portion of the alcoholic solution was evaporated and heated, as before, in a thin film.

8·385 grs. gave $\ddot{C}$ = 22·205, and $\dot{H}$ = 7·57 grs.

5. Of the resin thus analysed (4.) the remainder was again boiled in water. The first portion of water was not coloured, but acquired a very bitter taste; in the second portion employed, the taste was scarcely perceptible. Dried by heating for thirty-six hours at 180° Fahr., it was darker coloured than the resin first analysed, and when hot had a slight odour resembling ginger.

7·01 grs. gave $\ddot{C}$ = 18·56, and $\dot{H}$ = 6·37.

These two results are almost identical, giving per cent.,

	4.	5.	$C_{40}\ H_{33}\ O_7$, gives
Carbon	73·24	73·16	73·38
Hydrogen	10·00	10·01	9·88
Oxygen	16·84	16·83	16·74
	100	100	100

In the portion 3, therefore, the carbon is in excess to the amount of 0·6 per cent., either from an error of experiment, or from the presence of some impurity in the portion analysed, while the identity in constitution of the portions 4 and 5, shows either that the bitterness imparted to the water by boiling over specimen 4, was due to the solution of the resin itself, or that the quantity of the bitter substance it contained was too small to affect the results of analysis in any sensible degree.

6. It appears then that the resin obtained by digesting the crude labdanum of commerce in cold alcohol (0·83), is represented by $C_{40} H_{33} O_8$, while that obtained by the same means from the crude resin previously boiled in water $= C_{40} H_{33} O_7$. Is this difference owing to a species of transformation of the resin, or to the extraction by the water of a substance soluble both in water and alcohol?

To determine this point, I evaporated the bitter aqueous solutions obtained respectively by boiling the crude labdanum in water, and the substance extracted directly by alcohol from the crude resin. In both cases a small quantity of bitter extractive matter was left, which gradually attracted moisture from the air, but which was not subjected to any further examination. The presence of this substance had caused the difference between the results of the two series of analyses, and the close accordance of the first series with the formula $C_{40} H_{33} O_8$ is probably only accidental.

The pure resin of labdanum, therefore, may be considered as represented in constitution by the *irrational* formula $C_{40} H_{33} O_7$.

XII. *Berengela Resin.*

Under the name of Berengela resin or Berengelite*, I some time ago published a

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* The specimens of the substance for which I propose the name of Berengelite, were given to me by my friend Mr. Fryer, of Whitley House, near North Shields, and were obtained by him during his residence in South America. Of the circumstances under which it occurs, Mr. Fryer thus writes to me:—

"Of the resin or asphaltum from South America, I can unfortunately give you but a very imperfect account. I one day found in the yard of the Custom-house at Arica, a large convoy of llamas loaded with it, and all the information I could obtain from the men having charge of it was, that they brought it from St. Juan de Berengela, about 100 miles from Arica; that it was found in very large quantities, and formed, according to their description, something like a lake resembling the pitch lake of Trinidad. It is extensively used for paying boats and vessels at Arica, and, I believe, on the whole coast of Peru."

This substance is hard, brittle, may be scratched by the nail, has a resinous fracture and lustre, is of a dark-brown colour, with a tinge of green, but gives a yellow powder. The external appearance of the masses, as they were brought home, appears to indicate that the whole had formerly been in a softer state so as to yield easily to compression. It is insoluble in water, but dissolves readily and in large quantity in cold alcohol or ether, giving brown solutions. A small residue of earthy impurities is left. By evaporating the alcoholic solution, the resin is obtained of greater transparency, transmitting light of a bright-red colour, fusing easily on the water-bath, and remaining soft and unctuous at the ordinary temperature of the atmosphere. It gradually recovers its brittleness, but after the lapse of three or four months it is still soft, and adheres in some measure to the fingers. This property appears to be possessed by many other resinous substances, and explains the semifused appearance of the imported masses.

It has a peculiar, unpleasant, resinous odour. After fusion for some time at 212° Fahr., the unpleasant odour disappears, and is succeeded by an agreeable fragrance. On cooling again, it assumes, after some time, its original smell. When chewed in the mouth, it imparts a slight sensation of bitterness; but the alcoholic solution has a disagreeable very bitter taste.

Like most other resins, it is nearly insoluble in a concentrated solution of caustic potash. Boiled in a more dilute alkali it gives a yellow solution, from which the resin is again precipitated by acids. The alcoholic solution gives with a similar solution of acetate of lead, a copious yellow precipitate. It is, therefore, an acid resin. Its alcoholic solution is rendered milky by liquid ammonia, and passes milky through the filter.—London and Edinburgh Journal of Science, Third Series, vol. xiv. p. 89.

description of a substance, said to occur in large quantities as a mineral deposit at San Juan de Berengela, in South America. This fossil body is a true resin of a brown colour, giving with cold alcohol a brown solution, having a peculiar unpleasant odour, and a disagreeable exceedingly bitter taste.

In the same paper I inserted also two analyses of this substance, which gave per cent.,

	1.	2.	The formula $C_{40}H_{31}O_8$ gives	The formula $C_{41}H_{31}O_8$ gives
Carbon	72·47	72·34	72·04	72·53
Hydrogen	9·20	9·36	9·12	8·93
Oxygen	18·33	18·30	18·84	18·54
	100	100	100	100

The analytical results, when compared with the calculated numbers, show an excess of carbon above what is required by the formula containing C_{40}. Being, at the time when these analyses were made, unaware of the apparently universal prevalence of this quantity C_{40}, in the formulæ for the resins, which the present investigation seems to exhibit, I was by this excess led to adopt in preference the second formula containing C_{41}. On deducing for the resin of labdanum, however, as shown in the preceding section, a formula approaching very closely to that previously assigned to the Berengela resin, I was induced to return to the latter substance, and by a repetition of the analyses to test my previous results.

1. A small portion of the alcoholic solution was therefore evaporated, and the resin in the form of a thin film kept at a temperature of 150° Fahr. for twelve hours, and afterwards at 212° for two hours. The resin when cold was brittle, but the particles cohered slightly after standing for some time. Burned in the air it left 0·20 per cent. of brown ash.

A. 10·3 grs. gave $\ddot{C} = 27·26$, and $\dot{H} = 9·41$ grs.
B. 8·17 grs. gave $\dot{H} = 9·45$ grs., or per cent.,

	A.	B.	
Carbon	73·16		40 atoms
Hydrogen	9·43	9·45	31·6 atoms
Oxygen	17·41		7·3 atoms.
	100		

2. In the result A. the carbon is still more in excess than in the previously published analyses, and as the number of atoms seemed to indicate the formula $C_{40}H_{31}O_7$, I evaporated another portion, and exposed it in a still thinner film for twenty hours to a temperature, until the last two hours, not exceeding 200° Fahr. The resin thus obtained retained its natural pale colour and peculiar odour, melted at 212° Fahr., was brittle when cold, and when broken up its particles showed little tendency to cohere.

6·667 grs. (6·654 grs. pure resin) gave $\ddot{C} = 17·8$, and $\dot{H} = 5·62$ grains.

3. In order to ascertain the effect of a still more protracted heating, a further portion of the solution was evaporated in a thin film, and kept at 200° Fahr. for sixteen hours. The heating appeared in this instance to have produced incipient decomposition, the resin having acquired a slightly darker colour than the portions previously analysed.

In this state 6·865 grs. (6·852 grs. pure resin) gave $\ddot{C} = 18{\cdot}4$, and $\dot{H} = 5{\cdot}81$ grs.

The three results above obtained give respectively,

	1. 12 hours at 150°.	2. 20 hours at 200°.	3. 16 hours at 220°?	$C_{40}\ H_{31}\ O_7$ gives	$C_{40}\ H_{30}\ O_7$ gives
Carbon	73·16	73·98	74·25	73·63	74·00
Hydrogen	9·43	9·39	9·42	9·33	9·06
Oxygen	17·41	16·63	16·33	17·04	16·94
	100	100	100	100	100

From the appearances presented during the prolonged heating, I am inclined to consider the resin of 2 to have been nearly in the normal state, and that the portion 3 had been heated too long. The chief difficulty is in regard to the hydrogen, as considerable pains were taken in exhausting the moisture from the combustion tube. Considering, however, the comparatively low temperature at which the exhaustion must be performed, in order to prevent loss, in the case of a resin which melts so easily as the present, I am inclined to adopt the formula containing H_{30} as the safer of the two.

There is still therefore a relation between the Berengela and labdanum resins, the former being represented by $C_{40}\ H_{30}\ O_7$, and the latter by $C_{40}\ H_{33}\ O_7$.

XIII. *Resin of Retin-Asphalt.*

Having thus succeeded in bringing the Berengela resin within the dominion of our general formula containing C_{40}, I became desirous of ascertaining how far my present experience of the mode of obtaining the several resins in the normal state, might enable me to deduce for the resin of *Retin-Asphalt* a formula which would be included in the same general expression.

This resin is extracted by alcohol or ether from the mineral retin-asphalt of Bovey, of which it constitutes about sixty per cent. Evaporated at 212° the solution affords a light brown unfused resin, which begins to melt at 250° Fahr., is fluid at 300°, and at a temperature not exceeding that at which it becomes fluid, gradually decomposes. It is sparingly soluble in cold alcohol, more largely in boiling alcohol, from which it is partially precipitated on cooling. Ether dissolves it more easily and in greater quantity, giving a dark brown solution.

On a former occasion I published* two analyses of this resin, from which I deduced the formula $C_{21}\ H_{14}\ O_3$. Into this formula the constant C_{40} does not enter, as the analyses were made before the commencement of the present investigation had taught

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* London and Edinburgh Journal of Science, Third Series, vol. xii. p. 561.

me, either that this constant was to be looked for in the expression for a resinous substance, or the precautions necessary to be adopted in the extraction and drying of the resins themselves.

The following analyses not only rectify the formula, but show also the cause to which the deduction of an erroneous formula from the previous analyses is to be ascribed.

Retin-asphalt was treated with three successive portions of alcohol, being boiled with the last portion till everything soluble appeared to be taken up.

The resin left by evaporating each of these three portions in a thin film, and heating it at 200° Fahr. for twelve hours, was analysed separately. It was in the state of a light brown powder, or of a dark brown film.

Of one of these portions when burned in the air,

5·774 grs. left 0·04 grs. of gray ash = 0·7 per cent.

Of another 2·417 grs. left 0·021 grs. = 0·86 per cent., giving as a mean 0·78 per cent. of earthy matter in the resin after solution in the alcohol,

A. of the first portion 5·78 grs (5·735 grs. pure resin) gave

$\ddot{\mathrm{C}}$ = 15·74, and $\dot{\mathrm{H}}$ = 4·571 grs.

B. Of the second 7·624 grs. (7·565 grs. pure resin) gave

$\ddot{\mathrm{C}}$ = 20·865, and $\dot{\mathrm{H}}$ = 5·995 grs.

C. Of the third 5·88 grs. (5·834 grs. pure resin) gave

$\ddot{\mathrm{C}}$ = 16·01, and $\dot{\mathrm{H}}$ = 4·56 grs.

D. Of a mixture of these, heated till the resin began to melt and cohere, being when cold very dark brown and porous, 7·13 grs. (7·074 grs. pure resin) gave

$\ddot{\mathrm{C}}$ = 19·51, and $\dot{\mathrm{H}}$ = 5·445 grs.

E. Of the same fused at the lowest possible temperature for three hours, 7·805 grs. (7·744 grs. pure resin) gave

$\ddot{\mathrm{C}}$ = 21·87, and $\dot{\mathrm{H}}$ = 6·063 grs.

These results gave for the various portions the following constitution per cent.:

	Dried for twelve hours at 200° Fahr.			Afterwards heated to incipient fusion.	Kept at melting point for three hours.
	A.	B.	C.	D.	E.
Carbon	75·89	76·26	75·88	76·26	78·08
Hydrogen	8·85	8·80	8·68	8·55	8·70
Oxygen	15·26	14·94	15·44	15·19	13·22
	100	100	100	100	100

The formula $C_{40} H_{27} O_6$, gives

		Per cent.
40 Carbon	= 3057·48	76·53
27 Hydrogen	= 336·95	8·44
6 Oxygen	= 600·00	15·00
	3994·43	100

With this formula, the results of the first four analyses are accordant within the limits of the errors of manipulation. In the fifth analysis there is a large excess of carbon, obviously due to decomposition caused by the prolonged fusion.

The analyses previously published gave the following results:

	After prolonged heating at 212° FAHR.	After fusion at 300° FAHR.
Carbon	76·86	77·41
Hydrogen	8·75	8·51
Oxygen	14·39	14·08
	100	100

In both of these the carbon is in excess, though in neither is the excess so great as in the fifth analysis above given. It is, however, to be ascribed to the same cause, namely, to partial decomposition, though not carried so far.

From the above experiments, therefore, it appears,

1. That this resin, like many others we have examined, may be perfectly dried by heating at 200° FAHR. in the state of a thin film without being melted.

2. That when thus dried it may be represented by $C_{40}\ H_{27}\ O_6$; and

3. That when fused it rapidly decomposes, the per centage of carbon increasing, while that of hydrogen remains nearly stationary. The analysis E. gave

		$C_{40}\ H_{27}\ O_5$ gives
Carbon	78·08	78·51
Hydrogen	8·70	8·65
Oxygen	13·22	12·84
	100	100

So that by prolonged heating at the melting point the formula $C_{40}\ H_{27}\ O_6$ gradually approximates to $C_{40}\ H_{27}\ O_5$, which, as will appear in a subsequent part of this paper, is identical with the change which heat produces on some other resins, as the resin of assafœtida.

4. *Salts of this resin.*—In the paper to which I have already referred I have shown that an alcoholic solution of this resin precipitates similar solutions of nitrate of silver and of acetate of lead. The salt of silver appears to be represented by $2\,Ag\,O + (C_{40}\ H_{27}\ O_6)$.

XIV. *Ammoniac Resin.*

I. When the ammoniac resin of the shops is digested in cold alcohol, it undergoes little alteration in bulk, but a pale yellow solution is obtained, which on evaporation in a thin film at 150° FAHR. gives a transparent nearly colourless resin, having the characteristic odour of the natural product. Heated to 212° FAHR. for some time, the resin assumes a yellow colour, which gradually deepens, while at the same time the peculiar odour becomes less intense. After heating for forty-eight hours at 180° FAHR., and afterwards for several hours at 212° in a thin film,

A. 7·045 grs. gave $\ddot{C} = 18·29$, and $\dot{H} = 4·79$ grs.
B. 6·76 grs. gave $\ddot{C} = 17·62$, and $\dot{H} = 4·645$ grs.

These give per cent.,

	A.	B.
Carbon	71·78	72·07
Hydrogen	7·55	7·63
Oxygen	20·67	20·30
	100	100

The formula $C_{40}\ H_{25}\ O_9$, gives

		Per cent.
40 Carbon	= 3057·48	71·61
25 Hydrogen	= 311·99	7·30
9 Oxygen	= 900·00	21·09
	4269·47	100

which agrees so closely with the experimental results, that we are justified in adopting it as the probable formula for the resin. The two portions analysed exhibit a slight excess of carbon, which may be attributed to the too prolonged action of the heat. This is rendered more probable by the following analysis.

II. A portion of the resin, dried as above, was heated in a shallow platinum capsule over the lamp to a temperature of about 270° Fahr. for some hours, till it had almost entirely lost its characteristic odour. No frothing took place, nor were any visible fumes given off; it remained in quiet fusion, gradually assuming a greater consistence, and becoming of a darker shade of colour. In this state

A. 5·76 grs. gave $\ddot{C} = 15·2$, and $\dot{H} = 3·91$ grs.
B. 6·98 grs. gave $\ddot{C} = 18·37$, and $\dot{H} = 4·67$ grs.

or per cent.,

	A.	B.
Carbon	72·97	72·77
Hydrogen	7·55	7·43
Oxygen	19·48	19·80
	100	100

These results show that by a heat of 270° + this resin is gradually decomposed, the volatile matter which flies off containing more oxygen in proportion to the hydrogen than exists in the resin itself, while in some others belonging to the same natural group, as in the lump dragon's blood, the contrary is the case.

Thus deducting 0·23 from the hydrogen of analysis B. for hygrometric moisture, it becomes

Carbon	72·77	40 atoms
Hydrogen	7·20	24·24 atoms, and loss = 0·76 atoms
Oxygen	20·03	8·41 atoms, and loss = 0·59 atoms
	100	

the loss of the hydrogen being to that of the oxygen as 5 : 4, while in the resin they exist in the proportion of 8·3 to 3.

This resin is easily fusible, and like the Berengela and assafœtida resins, runs into a mass in the bottle in which it is kept. The alcoholic solution gives, with a similar solution of acetate of lead, a white precipitate, but I have not as yet analysed any of its salts.

XV. *Resin of Opoponax.*

The green resin of opoponax, treated with common alcohol, gives a pale brownish-red solution, from which, by evaporation, a transparent brown resin is obtained having a peculiar odour, fusing readily at 212° FAHR.; and after being kept at that temperature for a short time, becoming brittle when cold. The residue from the natural resin, after being treated with alcohol, gives with boiling water a solution which passes milky through the filter. Both solutions have a bitter taste, accompanied by a peculiar flavour. The matter which remains insoluble in alcohol or water consists chiefly of woody fragments, and is nearly equal in bulk to the natural gum resin originally experimented upon.

The resin extracted by alcohol is decomposed by a comparatively low temperature, and requires therefore to be treated with considerable care, when prepared for the purpose of analysis.

This is shown by the following experiments.

1. A small portion of the alcoholic solution was evaporated at a gentle heat, which, when the resin was nearly free from alcohol, was raised to 212° FAHR. It was kept at this temperature for two hours, but from the inclination of the shallow vessel a considerable portion of the resin (the whole not exceeding 10 grs.) had run together into a mass. On cooling, this latter portion did not harden. The brittle portion was scraped off the dish, and burned with oxide of copper.

$$7·5 \text{ grs. gave } \ddot{C} = 17·14, \text{ and } \dot{H} = 4·52 \text{ grs.}$$

2. A second portion of the alcoholic solution was evaporated at 150° FAHR., and the resin, in the state of a very* thin film, was kept twelve hours at a temperature not exceeding 180° FAHR. Previous to analysis the heat was raised for one hour to 212° FAHR. The resin was very brittle, in thin fragments, was of a pale brown colour, and preserved the characteristic odour.

$$7·995 \text{ grs. gave } \ddot{C} = 18·55, \text{ and } \dot{H} = 4·785 \text{ grs.}$$

3. A third portion being evaporated at a gentle heat was fused for two hours at 212° FAHR.

$$7·62 \text{ grs. gave } \ddot{C} = 17·64, \text{ and } \dot{H} = 4·633 \text{ grs.}$$

4. The resin of a fourth portion, after long exposure to a gentle heat, was fused for a few minutes at 250° FAHR.

$$7·69 \text{ grs. gave } \ddot{C} = 18·05, \text{ and } \dot{H} = 4·61 \text{ grs.}$$

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[*] A grain of the resin being spread over at least a square inch of surface.

5. A fifth portion after long heating at 212°, owing to the drying of the water-bath, was allowed to remain for some time at a higher temperature. Its colour was in some degree darker.

7·36 grs. gave $\ddot{C} = 17·67$, and $\dot{H} = 4·50$ grs.

These results give per cent. respectively,

1. At 212° for a short time.	2. 12 hours at 180° and 1 hour at 212°.	3. 2 hours at 212°.	4. Fused at 250°.	5. Half an hour at 250° ±.
Carbon 63·21	64·15	64·01	64·90	66·38
Hydrogen 6·66	6·66	6·75	6·66	6·79
Oxygen 30·13	29·19	29·24	28·44	26·83
100	100	100	100	100

From the mode in which these several specimens of resin were prepared, it is obvious that Nos. 2 and 3 represent most nearly the normal state of the resin. In No. 1 so much of the volatile matter remained as to prevent the resin from entirely concreting; while in 4 and 5 the heat had been raised, or prolonged, so as to cause partial decomposition. The formula $C_{40}\ H_{25}\ O_{14}$, gives

		Per cent.
40 Carbon	= 3057·480	64·15
25 Hydrogen	= 311·99	6·52
14 Oxygen	= 1400·000	29·33
	4769·47	100

which agrees very closely with the results of the second and third analyses, while those of the first and fourth analyses oscillate on either side of the calculated numbers. We seem to be justified therefore in adopting this formula for the constitution of the resin of opoponax, as it exists in the natural gum resin of commerce.

In reference to the analyses 4 and 5 above given, I would draw attention to a fact which may hereafter prove of considerable consequence when we come to consider the rational constitution of the resins. It will be observed that, by an increase of temperature, sufficient to produce partial decomposition, the carbon increases, while the per centage of oxygen decreases almost in equal proportion, that of the hydrogen remaining nearly constant. This was the case also as above shown with the resin of retin-asphalt, and approximately also with that of ammoniac, and we shall have occasion to make the same remark in regard to several other resins to be treated of in the following sections. I may mention, especially that of assafœtida, with the analysis of which I propose to conclude the present part of these researches.

The nature of this action of an elevated temperature is shown more clearly by comparing the *atomic* constitution of the resin before and after being heated. Thus the fifth analysis of the resin of opoponax gives

Carbon	66·38	4 atoms.
Hydrogen	6·79	25·09 atoms.
Oxygen	26·83	12·4 atoms.
	100	

by which we see that the oxygen diminishes much more rapidly than the hydrogen; that water or a carbo-hydrogen are not alone given off, but along with these, if evolved at all, there is evolved another substance also of more complicated constitution.

XVI. *Resin of Assafœtida.*

I. The assafœtida of the shops loses little in bulk when digested in cold alcohol of 0·83, but it gives a pale-yellow solution, from which, by evaporation, a resin of the same colour is obtained. This resin has the characteristic odour of the gum resin, and the property which the natural product also possesses of becoming purple when exposed to the sun's rays. Laid as a thin coating upon paper, the pure resin is much more sensible to the sun's rays than the resin of guiacum, and affords a much more beautiful colour. It is readily and completely soluble in cold alcohol and ether. Like many other resins it must be heated for a length of time before it becomes hard and brittle, and reaches its normal state. By this prolonged heating it acquires a darker and brownish colour, and is easily decomposed if the temperature be raised much above 212° Fahr. As the temperature rises, the resin froths up very much for some time, giving off a strong garlic odour; it then flows quietly till the heat is again increased. When completely burned, the resin employed in the following analyses left 0·18 per cent. of brown ash.

1. A small portion of the solution was evaporated and heated in the state of a thin film for forty-eight hours to 180° Fahr., and afterwards for six hours to 212° Fahr. The resin was brittle.

$$5·79 \text{ grs. gave } \ddot{C} = 14·52, \text{ and } \dot{H} = 3·93 \text{ grs.}$$

2. A second portion was evaporated and digested for many hours at 212° Fahr.

$$8·19 \text{ grs. gave } \ddot{C} = 20·66, \text{ and } \dot{H} = 5·55 \text{ grs.}$$

3. Of the same, a portion heated twelve hours longer, and from that cause a little darker in colour,

$$6·02 \text{ grs. gave } \ddot{C} = 15·32, \text{ and } \dot{H} = 4·14 \text{ grs.}$$

4. Of the same mass, a portion was heated very gently in a platinum capsule over a lamp, and kept in a state of fusion for an hour. The heat was not sufficient to drive off any visible fumes, but the odour of the resin became much weaker. In this state

$$6·56 \text{ grs gave } \ddot{C} = 16·82, \text{ and } \dot{H} = 4·475 \text{ grs.}$$

These results, allowing 0·2 per cent. for foreign matter, are equal to

	Heated 48 hours at 180 and 6 hours at 212° FAHR.	Heated long at 212° FAHR.	Heated 12 hours longer at 212° FAHR.	Heated over the lamp 1 hour at 220°
Carbon	69·49	69·90	70·51	71·05
Hydrogen	7·56	7·55	7·65	7·59
Oxygen	22·95	22·55	21·84	21·36
	100	100	100	100

The formula $C_{40}\ H_{26}\ O_{10}$, gives

		Per cent.
40 Carbon	= 3057·48	69·75
26 Hydrogen	= 324·47	7·44
10 Oxygen	= 1000·00	22·81
	4381·95	100

These numbers agree very closely with the result of the second analysis, and do not deviate much from the numbers deduced from the first and third analyses. For other reasons, besides this accordance, I am inclined to consider the portion employed in the second analysis as approaching nearest to the normal state of the resin, and have, therefore, no reason at present to doubt that the formula $C_{40}\ H_{36}\ O_{10}$, represents very nearly the true constitution of the resin as it exists in the crude assafœtida of commerce.

II. If we compare with each other this formula and that deduced for the resin of ammoniac, from the analyses above given, we observe that they differ only in the presence, in assafœtida resin, of the elements of one atom of water more than are contained in the ammoniac resin. Thus

$$\begin{array}{lcl} \text{Assafœtida resin} & = & C_{40}\ H_{26}\ O_{10} \\ \text{Ammoniac resin} & = & \underline{C_{40}\ H_{25}\ O_{9}} \\ \text{Difference} & & \quad H_{1}\ O_{1} \end{array}$$

On this coincidence I believe little reliance is to be placed, inasmuch as in neither resin is the number of atoms of hydrogen to be considered as *certain*; it nevertheless suggests the inquiry—can any number of these resins be hydrates of a common radical, or does water as such enter into their constitution? In so far as the direct application of heat is concerned, we have already seen*, in the case of opoponax and ammoniac resins, that when the temperature is increased so as to cause incipient decomposition, the elements are not given off in such proportion as to form water only. Water may be one of the products of the decomposition by heat, but if it existed as such in the resin, why should other products be always evolved along with it?

By comparing the relative atomic proportions of the elements as obtained in the four analyses of assafœtida resin above detailed, we shall be satisfied that though the

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* See pp. 351 and 353.

resins appear to be so related, yet that of assafœtida is not be considered as a hydrate of the resin of ammoniac. Thus the

	Carbon.	Hydrogen.	Oxygen.
First analysis gave	40 atoms.	26·7 atoms.	10·18 atoms.
Second	40 atoms.	26·4 atoms.	9·96 atoms.
Third	40 atoms.	26·6 atoms.	9·55 atoms.
Fourth	40 atoms.	26·2 atoms.	9·3 atoms.

Now, allowing a similar error in the hydrogen in the four analyses, we see that the hydrogen and oxygen by no means diminish in the ratio in which they enter into the constitution of water. Taking No. 2 as the normal state of the resin, we find that in No. 4 the loss of hydrogen was 0·2 of an atom, while that of oxygen was 0·66, or three times as much as was necessary to form water with the hydrogen. In the volatile substance which escapes during the heating, therefore, the oxygen is to the hydrogen in atoms as 3 : 1, while in the resin itself they are nearly as 2 : 5. We have seen that in ammoniac and opoponax resins, the volatile matter given off in heating to incipient decomposition, also contains more oxygen in proportion to the hydrogen than exists in the resin itself.

III. As the resin, when heated gently over the lamp, and kept for a length of time in fusion, approached in composition to a formula containing nine of oxygen (see fourth analysis above), I heated a second quantity very gently under the same circumstances, and kept it in fusion for six hours; there was no frothing; the resin nearly lost its smell, and became slightly darker in colour. It was more brittle, and the fragments showed still less tendency to cohere than before.

6·42 grs. (6·407 grs. pure resin) gave $\ddot{C}$ = 16·535, and $\dot{H}$ = 4·425 grs., or per cent.,

Carbon	71·37	40 atoms.
Hydrogen	7·66	26·3 atoms.
Oxygen	20·97	9·05 atoms.
	100	

This result is in exact accordance with those of the other analyses, and with the remarks already made in regard to the comparative rapidity with which the oxygen diminishes. For while the analysis of the resin in its normal state (No. 2) gave

	Carbon.	Hydrogen.	Oxygen.
	40 atoms.	26·4 atoms.	9·96 atoms,
we have now obtained	40 atoms.	26·3 atoms.	9·05 atoms,

so that by prolonged fusion at a temperature of about 250°, till it nearly loses its smell, the resin $C_{40} H_{26} O_{10}$ changes into $C_{40} H_{26} O_9$. The changed resin is still easily and completely soluble in cold alcohol of 0·84.

IV. We have seen that the alcoholic extract of the labdanum of commerce may be represented by $C_{40} H_{33} O_8$, and that by boiling in water a resin $C_{40} H_{33} O_7$[*] is obtained;

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[*] See under labdanum resin, p. 345.

this is precisely analogous to the change effected as above, by heating the resin of assafœtida. With the view of ascertaining how far mere boiling in water would produce this change upon assafœtida, I digested a portion of the crude resin of commerce in alcohol, poured the filtered alcoholic solution into a large quantity of boiling water, and boiled the mixture for an hour. Along with the alcohol a volatile oil escaped into the atmosphere, which diffused a powerful odour through the room, and which as it came forth from the mouth of the flask affected the eyes, like the fresh juice of the onion. After this prolonged boiling the smell nearly disappeared, and on cooling the solution, the greater part of the resin subsided slowly in the form of a yellow powder, the supernatant liquid remaining turbid for many days. The yellow powder dissolved readily, largely, and without residue, in cold alcohol. Evaporated and heated to 212° Fahr. for eight hours in a thin film, it gave a resin which at first was rapidly coloured by exposure to the light, and by the prolonged heating acquired a decidedly reddish brown colour.

6·5 grs. (6·487 grs. pure resin) gave $\ddot{C} = 16·76$, and $\dot{H} = 4·485$, or per cent.,

Carbon	71·43
Hydrogen	7·68
Oxygen	20·89
	100

This result agrees almost exactly with that yielded by the resin after long heating over the lamp, and like it agrees with the formula $C_{40} H_{26} O_9$.

I refrain at present from discussing the question which suggests itself—whether we ought to consider the resin thus boiled and heated, or as it is obtained directly from the natural product by means of alcohol, to be in its normal state; or whether the presence of a quantity, perhaps variable, of a volatile oil be the only source of the different formulæ deduced from the analyses of the resin in its two states? This and other questions of a similar character will find their true solution as our investigation proceeds, and our knowledge of the constitution, mutual relations, and transformations of the resins becomes more extended.

The solution of the crude resin of assafœtida in alcohol gives a bulky, white, curdy precipitate, with an alcoholic solution of acetate of lead. I have analysed this salt, but the result is such as, with other similar results, to indicate the necessity of an extended inquiry into the constitution of the salts of this and the other resins. This inquiry I propose to enter upon on a future occasion.

Note.—The odour of this resin suggests the possibility of its containing sulphur as a constituent. Boiling nitric acid dissolves the resin completely, with evolution of red fumes, but the solution diluted with water and filtered, gave no trace of a precipitate with chloride of barium. It was burned also by projecting it in small fragments into a flask containing a fused mixture of chlorate of potash and common salt. The mixed salts were afterwards dissolved, but no milkiness was occasioned by chloride of barium.

General Remarks.

At the close of the former Part (III.) of these researches, I stated that a slight change in the general formulæ we had seen reason to adopt, as representations of the constitution of the resins, would be rendered necessary by certain analyses which I had already made, but which were not in a state for publication. Some of these analyses are contained in the present paper, and I shall here shortly advert to the modifications they suggest.

I. As a general expression for all the resins of which the composition was then known, I proposed the irrational formula $C_{40}\,H_{32-x}\,O_y$, in which x varied from 0 to 12, and y from 1 to 12. No resins were then known which had been shown with any degree of certainty to contain more than thirty-two of hydrogen to forty of carbon.

II. Observing also that those resins in which the hydrogen was less than twenty-four atoms possessed physical and chemical properties analogous to each other, yet remarkably distinct from those exhibited by the resins in which the hydrogen approached to thirty-two atoms, I was induced to subdivide the resins into two sections, represented respectively by

$C_{40}\,H_{32-x}\,O_y$, of which colophony is to be regarded as the type; and
$C_{40}\,H_{24-x}\,O_y$, of which gamboge and dragon's blood are members.

III. In the present paper, however, are introduced three resins, those of scammony ($C_{40}\,H_{33}\,O_{20}$), jalap ($C_{40}\,H_{34}\,O_{18}$) and labdanum ($C_{40}\,H_{33}\,O_7$), in which the hydrogen exceeds thirty-two atoms. To include these, therefore, our first *sectional* formula must be modified by the insertion of the plus (+) after 32, giving it the form

$$C_{40}\,H_{32\pm x}\,O_y,$$

in which state it includes the three resins above-mentioned, in which the hydrogen is present in greater quantity.

It may, perhaps, become a question hereafter whether these resins ought not to be placed in a separate section, represented by $C_{40}\,H_{32+x}\,O_y$, since their properties, and especially their action upon the system, is so very different from that of any of the resins of the pine tribes, of which colophony is the type. This point, however, will become more clear after the other resins usually classed by systematic writers along with those of scammony and jalap have been examined and analysed.

In connexion with this alteration in our formula deduced from the analyses above given, I ought to advert to two formulæ *for the crystallized resin of elemi*, lately published by Professors Hess of Petersburgh and H. Rose of Berlin*. The former chemist assigns to this resin the formula $C_{40}\,H_{33}\,O$, and the latter $C_{40}\,H_{34}\,O$, differing only in regard to the presence or absence of one atom of hydrogen. Whichever of these formulæ be adopted, the change above introduced into our general expression

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* See Poggendorff's Annalen, vol. xxxiii. p. 51; vol. xlvi. p. 322; vol. xlvii. p. 61; vol. xlix. p. 219.

would be rendered necessary had we not been previously led to it by the resins, of which the analysis is given in the present paper.

I have frequently had occasion in the course of this investigation to advert to the difficulty I have experienced in deciding which of two numbers to adopt as representing the equivalents of hydrogen in a given resin, and to state how very little reliance I could myself place on the exactitude of the numbers I was induced to prefer as the most probable. There are, apart from errors of manipulation, difficulties in the way of these analyses, arising from the presence of volatile matter in some of the resins, and from the ease with which others are decomposed, which make me willing to distrust my own formulæ to the extent of one atom of hydrogen at least in each. I am not surprised, therefore, at the different results obtained by the distinguished chemists above-named in regard to the crystallized elemi resin, nor do I consider that the error, on whichever it may rest, is to be attributed to any want of dexterity in either of these excellent manipulators, but rather to the nature of the resin itself, and to the manner or length of time during which it has been previously heated.

IV. The analyses contained in the present paper exhibit the necessity also of a similar change in our second sectional formula, $C_{40}\,H_{24-x}\,O_y$. The resins of ammoniac and opoponax contain twenty-five, that of assafœtida twenty-six, and that of retin-asphalt twenty-seven atoms of hydrogen, while the latter alone approaches in any of its properties to the resins of the colophony type. Without inquiring closely, therefore, where the limits of the two groups are to be placed, I propose at present to insert the sign plus in this formula also, with the view of including in it the resins above-named, leaving to a future opportunity the discussion of the precise place in our groups or sub-groups which any particular resin ought to occupy.

Our general expressions, therefore, now assume the form of

$C_{40}\,H_{32\pm x}\,O_y$ for the first group, and of
$C_{40}\,H_{24\pm x}\,O_y$ for the second group.

To these irrational expressions I would not be understood as annexing any *permanent* value. They are intended merely to symbolize the present state of our knowledge on this subject. New researches will necessarily introduce modifications, and make us acquainted at length with expressions much more general, and assuming perhaps a different form.

V. In reference to the points of theory, with a view to the determination of which the present inquiry was undertaken, as stated at the commencement of this series of papers, we are already prepared I think to infer, that the resins are not all derivable from one common radical. Whether we are to consider the members of each of our great groups as compounds of a common radical, or the members of those sub-groups only, in which the atoms of hydrogen are constant while those of the oxygen vary, —whether the radical they contain be a binary compound of carbon and hydrogen, or ternary, and contain oxygen; whether the resins in general be simply oxides of such radicals, or hydrates containing the elements of water in a state of direct combination; or whether they be not rather formed by the union of two or more compound oxides; these are questions the greater number of which we are as yet far from being prepared to discuss with any chance of arriving at the truth. I waive, therefore, the consideration of all these points for the present, in the hope that light will spontaneously break in upon many of them, when in a succeeding part of this research I shall study the relations of the resins to the most important chemical reagents.

One important point may be considered as nearly established by the analyses already made, namely, that the constant C_{40} is *characteristic* of the irrational formulæ for this group of natural productions; and it is interesting to find that in exhibiting such a characteristic, it bears a striking resemblance to other groups, not very distantly allied to it, either in the physical properties they possess, or the natural sources from which they are obtained. I refer especially to the fixed and volatile oils, in many of the known formulæ for which a similar constant C_x is to be traced, and in which the number represented by x may be considered as characteristic of a more or less extensive natural group. I shall have an opportunity of illustrating this observation in a future paper.

Durham, March 13, 1840.