LXII.—CONTRIBUTIONS FROM THE LABORATORY OF
GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. VI. *On Essential Oil of Sage.*

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Chemistry.

Two papers have already been published by me, in conjunction with Sigiura, on "Essential Oil of Sage" (see *Phil. Mag.*, Nov., 1877, and this Journal, 1878, *Proc.*, 292). The present paper contains an account of investigations made with the view of supplementing the information detailed in the papers referred to, and at the same time of giving a general account of essential oil of sage, so far as the facts gained enable such an account to be given.

1. The sage plant grows wild in quantity in the south of Europe, especially in Dalmatia, in parts of Italy, and in the department of the Alpes Maritimes in France. The plant is also cultivated in the neighbourhood of Grasse (Alpes Maritimes), near Leipzig, and in Thuringia. The plant is cut in the autumn and placed at once in stills along with water, the distillate is returned to the stills, and this process is repeated several times in succession. The Italian wild sage yields from

1 to 1.25 per cent. of oil, the Dalmatian and that cultivated around Leipzig about 0.5 per cent., while from the French plant only about 0.3 per cent. of oil is obtained.

I have had a quantity of the leaves of the English sage plant distilled for me by Messrs. Wright, Layman and Umney, but the yield of oil amounted only to 0.07 per cent. The oil obtained from the French plant is of a pale-yellow colour, that distilled at Leipzig is reddish-brown, sometimes inclining to a greenish shade. The smell of the French oil is sharper, and at the same time more sickly than that of the German.

Two samples of English oil were specially distilled for me; that distilled in summer was yellow-brown to dark-brown, whilst that distilled in winter had a distinctly green shade.*

The composition of the English oil was somewhat different from that of the oil distilled at Leipzig.

2. The oil with which I worked was obtained through Messrs. Wright, Layman and Umney; it was distilled by Messrs. Sacchse of Leipzig in the summer of 1877.

In previous papers (*loc. cit.*) it has been shown that the main constituents of sage oil are—1. Two hydrocarbons, each having the formula $C_{10}H_{16}$, boiling at about 156° and 167° respectively. 2. An oxidised compound, *salviol*, probably $C_{10}H_{16}O$, boiling at about 200° . 3. A camphor, $C_{10}H_{16}O$. 4. Probably a few per cents. of cymene. And 5. In the oil distilled from the leaves of English grown sage, a hydrocarbon boiling at about 260° and having the formula $C_{15}H_{24}$.

3. The results obtained by the distillation of sage oil since the date of these papers require that certain modifications be made in the preceding statement.

That specimen of sage oil which was employed in the experiments described in *Phil. Mag.*, Nov., 1877, was of unknown age and origin; it was comparatively rich in camphor, contained very small quantities of the oxidised liquid constituent, *salviol*, moderate quantities of the $C_{10}H_{16}$ hydrocarbons, and a small quantity of what was described as "a dark-brown liquid with distinct fluorescence," boiling about 240° . This last-named liquid undoubtedly contained *cedrene*, $C_{15}H_{24}$.

The sample of oil examined in 1877–78 (this Journal, *loc. cit.*) was of German manufacture, and had not been distilled more than three months before the time when it was examined. It yielded moderate quantities of *salviol*, very little camphor, considerable quantities of the $C_{10}H_{16}$ hydrocarbons, and apparently no *cedrene*.

* For these details, and for specimens of sage plants and samples of German and French oils, I am indebted to the kindness of Mr. Umney, of Messrs. Wright, Layman and Umney, Southwark Street, to whom I wish to return my best thanks.

The sample with which I have now worked was a portion of that distilled in 1877, that is, two years before it was examined. This oil contained smaller quantities of $C_{10}H_{16}$ hydrocarbons than when it was last examined, but very much larger quantities both of salviol and camphor, and it also contained a considerable amount of cedrene, boiling at 260° .

It is very difficult to give any estimate of the quantities of the various constituents in any sample of sage oil, inasmuch as the oil is largely decomposed on distillation, but I should think that, roughly speaking, the latest examined sample contained about 40 per cent. of salviol, 10 per cent. of camphor, 20 per cent. $C_{10}H_{16}$ hydrocarbons, and 5 per cent. of cedrene ($C_{15}H_{24}$), the residue consisting of water and resin, non-volatile at 300° .

The sample of English-distilled oil formerly examined consisted of two portions, much the larger of which was distilled almost immediately before it was examined. The sample with which I now worked had been distilled six months before the examination was commenced.* The amount of $C_{10}H_{16}$ hydrocarbon in the former sample was about 5 per cent., in the latter about 2 per cent.; both samples consisted mainly of cedrene, but the latter (*i.e.*, the older) sample contained small quantities (perhaps 0.5 to 1 per cent.) of oil, distilling at about 200° , and having a pronounced odour of salviol. Neither sample yielded any camphor.

Now these general results undoubtedly show that the composition of sage oil varies according to the age of the sample. When first distilled the German oil is rich in hydrocarbons of the formula $C_{10}H_{16}$, contains a moderate amount of salviol, and little or no camphor; as the oil ages the amounts of salviol and of camphor increase, whilst a hydrocarbon, or hydrocarbons, of the formula $C_{15}H_{24}$ is produced. If the earliest examined sample may be regarded as a type of very old oil, then the amount of camphor in such oil is large, whilst the salviol is much reduced in quantity. I have also found that a sample of salviol prepared in the summer of 1878 contained from 2 to 4 per cent. of camphor after the expiry of 12 months. The effect of time on the composition of sage oil is therefore to increase the oxidised constituents at the expense of the $C_{10}H_{16}$ hydrocarbons, and simultaneously to produce higher isomerides of these compounds; and further, as the camphor in the oil increases in quantity the oxidised liquid constituent diminishes.

The same general results may be deduced from the examination of the two samples of English-prepared oils, but as the main constituent

* The specific gravity of English-distilled oil was given as 0.9258 at 17° ; but this oil contained a little water. I now find the specific gravity at 15° referred to water at the same temperature, to be 0.9325.

of these oils, when distilled, is a cedrene, the change of $C_{10}H_{16}$ to an oxidised compound is not so marked as in the case of the German oils.

The richness of the English oil in cedrene may be due to the fact that it was distilled wholly from the leaves of the plant.

4. Two small quantities of $C_{10}H_{16}$ hydrocarbons, boiling respectively at 156° and 167° , distilled from sage oil in 1877, and which had therefore remained in stoppered bottles containing air for two years, were submitted to fractional distillation. The greater part of each resinised; on decomposing these resins with water, separating the oil, drying, and distilling, about 20 per cent. of the 156° compound, and towards 50 per cent. of that formerly boiling at 167° , was obtained as a yellowish oil, boiling from 185° to 205° , and having a pronounced smell of salviol.

A small quantity of hydrocarbon distilled in 1876 (b. p. = 157°) was found, after three years' standing in a stoppered bottle containing air, to have resinised to a thick viscid liquid mixed with a small amount of solid matter.

This was dissolved in alcohol and the solution poured into water; a semi-solid oil separated, smelling exactly like turpentine oil, and a very small quantity of a white solid gathered at the bottom of the vessel.

These results show that the probable action of time and exposure on the $C_{10}H_{16}$ sage hydrocarbons is to produce first the liquid compound salviol, and then the solid camphor.

5. I have always found that when the *pure* hydrocarbon, $C_{10}H_{16}$, *pure* salviol (see par. 9), or *pure* cedrene is heated, no resination occurs. Further, these compounds when pure are not altered by exposure to light, whereas a mixture containing the same compounds is quickly darkened. (Sage oil itself, when kept in a colourless bottle, *very slowly* darkens in colour.)

As will be shown hereafter (par. 9), when salviol is heated, a small portion of it undergoes decomposition with production of water, and a hydrocarbon which very quickly darkens in colour and polymerises, a portion of the salviol also itself polymerising; but if the products of the very slight decomposition of the salviol be immediately removed the remainder of that compound may be boiled without change.

An investigation of the conditions of equilibrium of the chemical systems presented to us in the various essential oils would undoubtedly lead to most interesting results. Looked at generally, these conditions appear to be more in keeping with the so-called "Kinetic theory of chemical action," viz., that all systems of heterogeneous molecules tend to undergo continuous chemical changes, than with any other theory hitherto propounded.

6. In former papers it has been stated that sage oil contains two hydrocarbons of the formula $C_{10}H_{16}$, one boiling at 157° and identical with the terpene of French turpentine oil, the other boiling at or about 168° .

The 157° terpene obtained from the samples of oil examined in 1876-77 was lævogyrate, that separated from the German oil, soon after distillation, was dextrogyrate. The specific gravities and refraction equivalents of the two terpenes were practically identical.*

The results of an examination of the terpene from the present sample of German oil, *i.e.*, from oil two years after distillation, confirm those of previous papers.

There can be no doubt that sage oil contains a terpene, *i.e.*, a hydrocarbon of the formula $C_{10}H_{16}$, boiling at 156 — 157° . But does the oil contain an isomeride boiling at about 168° ?

That portion of the original distillate which came over below 190° was submitted to a prolonged fractionation over sodium, using Le Bel's apparatus. After about four weeks' continuous fractionation I was obliged to confess that the result was still doubtful. The hydrocarbons were, it seemed, oxidised by the action of sodium and air simultaneously with the reduction of the oxidised constituents of the oil; the hydrocarbons were also polymerised and resinised. I am convinced that, unless one works with very large quantities of material, long continued processes of fractionation of compounds of the terpene group, especially when mixed with oxidised derivatives such as salviol, are of little value. I succeeded, however, in splitting up what had formerly been regarded as a distinct hydrocarbon, boiling at 168° into a portion consisting of terpene, and another portion boiling at about 171° , but whether this would not itself be further decomposed if it were fractionated in quantity I cannot pretend to determine.

The supposed hydrocarbon boiling at 168° examined in 1876-77 (*Phil. Mag., loc. cit.*) undoubtedly contained salviol (see *sp. gr.*, action of heat, refraction equivalent, and odour).

That described in 1878 in this Journal was probably much purer, but it may have been a mixture. It has been already stated that pure English-distilled oil yielded about 5 per cent. of a hydrocarbon boiling at 166 — 171° ; the second sample obtained from the same source yielded about 2 per cent. boiling at about 170° .

These two liquids were mixed and again fractionated, and about 5 c.c. of a colourless oil boiling from 170 — 171° was obtained. From the physical data determined for this liquid (see Appendix, p. 690), and

* The figure given as the specific gravity of the terpene in the paper by Sigiura and Muir (this Journal, 1878; *Proc.*, p. 292), is a *lapsus pennæ*; it should have been 0.8635, not 0.8435.

from those determined for the similar liquid obtained from the German oil, it seems probable that sage oil does contain an isomeride of terpene, boiling somewhere about 170° — 175° .

This liquid, as also the terpene boiling at 156° , gave the reactions for dihydrochloride by Ribau's test. The comparative difficulty with which the dibromide, obtained by adding bromine to the liquid boiling at about 170° , is decomposed on distillation (*Phil. Mag., loc. cit.*), as also the production of oxalic acid by oxidising this liquid with dilute nitric acid, tend, on the whole, to confirm the supposition that sage oil contains an isomeride of terpene. The fractionation of large quantities of oil boiling at about 170° can, however, alone determine the existence or non-existence of the supposed hydrocarbon. Until certain of the actual existence of such a compound I forbear to add *salvene* to the already too long list of isomerides of terpene.

7. I now proceed to detail the results of the examination of the individual constituents of sage oil. The chemical work done was almost entirely confined to experiments with salviol and sage camphor.

The action of phosphoric anhydride, phosphorus pentachloride, and of bromine on salviol, has been examined; but as the quantities of material at my disposal were comparatively small, I shall give only the general results of the action, omitting all details of fractionation, &c.

Salviol, when heated with an excess of phosphoric anhydride for a considerable time, was resinised, with the exception of about one-fourth of the quantity originally used. The non-resinised portion consisted chiefly of a $C_{10}H_{16}$ hydrocarbon, boiling at about 172° , and probably identical with the hydrocarbon of this formula, and boiling about this point, which experiments indicate to be existent in sage oil. A small quantity of a paraffin-like hydrocarbon, which was unacted on by strong sulphuric acid, was also produced; this was probably identical with the $C_{10}H_{20}$ hydrocarbon obtained by Armstrong and Tilden by the action of sulphuric acid on French and American turpentine (this Journal, 1879; *Trans.*, p. 733), and by the former of these chemists by the action of iodine on camphor (*Ber.*, **11**, 151). The lower boiling fractions contained a very small quantity of a hydrocarbon, which was shown by its qualitative reactions to be, almost certainly, a benzene.

The resinous product of the action was unacted on by sodium, and appeared to be free, or nearly free, from polymerides of salviol, but to consist mainly of polymerides of $C_{10}H_{16}$; it was almost unacted on by concentrated sulphuric acid, and was non-volatile in steam. No cymene was found in the product of the action of phosphoric anhydride on salviol.

These results almost oblige us to regard salviol as $C_{10}H_{16}O$, and not as $C_{10}H_{16}O$, as formerly supposed.

Phosphorus pentachloride exerted no action on salviol at ordinary

temperatures. On heating the two substances together hydrochloric acid was evolved, and a dark-coloured oil was obtained, which could not be distilled without decomposition. On repeated distillation over sodium this oil yielded a $C_{10}H_{16}$ hydrocarbon, boiling at a temperature higher than 157° , and a small quantity of a hydrocarbon, other than cymene, boiling about 170° , and unacted on by concentrated sulphuric acid.

Bromine acted on salviol with evolution of much hydrobromic acid and production of considerable quantities of a yellow-red oil, which was decomposed on distillation with separation of carbon. It has been before shown (Sigiura and Muir, *loc. cit.*) that under certain conditions a brominated derivative of salviol is obtained, which on exposure to air slowly deposits crystals of camphor. From the reaction of the brominated oil now obtained it is very probably an addition-product, and the production of camphor from this oil may be represented as $C_{10}H_{18}Br_2O = C_{10}H_{16}O + 2HBr$.

8. The production of camphor melting at 174° by oxidising salviol with chromic liquor has been fully confirmed. The ready oxidation of salviol to camphor explains the fact that the amount of camphor in sage oil increases as the oil ages.

I was for some time inclined to believe that camphor was produced during the fractionation of those portions of the oil boiling about 200° , but careful experiments with oil from which no camphor separated at -15° , have shown that this is not the case. That the prolonged action of air and diffused sunlight on salviol, even at ordinary temperatures, does, however, convert a portion of it into camphor is evidenced by the fact that salviol, which in the summer of 1878 was free from camphor, contained about 3 per cent. of this substance in the summer of 1879.

The production of an oil (noticed in a former paper) by treating salviol with nitric acid, which on decomposition with water yielded camphor, is evidently to be traced to the secondary action of the acid on the camphor produced; inasmuch as I find that sage camphor is dissolved by 1 : 1 nitric acid, and that addition of water to the yellow oil so formed causes a reprecipitation of camphor.*

9. When perfectly dehydrated salviol was boiled it suffered very slight decomposition with production of a little water and slight darkening in colour, but by far the greater portion distilled unchanged. The slightly darkened oil was shown to contain traces of polymerised substances, probably polymerides of salviol and of $C_{10}H_{16}$ hydrocarbons; not a trace of cymene was found.

This reaction, as well as the production of camphor by oxidising salviol, points to the formula $C_{10}H_{18}O$.

* This reaction may be advantageously applied to the purification of sage camphor.

10. In a former paper (*Phil. Mag., loc. cit.*) the results of two combustions of salviol were detailed, giving respectively, *hydrogen*, 10·31 and 10·67; *carbon*, 78·83 and 78·86 per cent.

Mr. Alfred J. King, of the Owens College, has been so good as to make several combustions of salviol apparently free from camphor, and boiling at 200—201°; his results are annexed:—

		Gram H ₂ O.		Gram CO ₂ .	
1.	0·2685 gram gave		0·2620	—	
2.	0·1665 " "		0·1686	0·4785	
3.	0·3035 " "		0·2905	0·8735	
4.	0·3030 " "		0·2895	0·8730	
5.	0·2570 " "		0·2515	0·7390	

Calculated for		Found.					
C ₁₀ H ₁₆ O.	C ₁₀ H ₁₈ O.	I.	II.	III.	IV.	V.	Mean.
Carbon ..	78·94 77·92	—	78·37	78·49	78·58	78·42	78·46
Hydrogen	10·52 11·68	10·84	11·24	10·63	10·62	10·87	10·84

Difference of mean from		
	C ₁₀ H ₁₆ O.	C ₁₀ H ₁₈ O.
Carbon	—0·48	+0·54
Hydrogen	+0·32	—0·84

If these numbers be compared with those formerly obtained, the carbon is found to be now 0·38 lower, and the hydrogen 0·34 higher than then.

Regarding the reactions of salviol already described, I think that the conclusion appears inevitable that this compound should be formulated C₁₀H₁₈O. The discrepancies between the above numbers and those calculated from this formula are most probably due to the retention by the salviol of small quantities of camphor.

11. Camphor separates from sage oil chiefly from the fraction boiling between 205° and 208°; it is partially soluble in salviol, but separates almost completely therefrom at —15°.

The melting point of sage camphor, after eight sublimations, was found to be 174°, and the boiling point 205° (both uncorr.), *i.e.*, the same as those of laurel camphor.

Phosphorus pentachloride readily acted on sage camphor with production of an oil, which was decomposed by water, yielding a wax-like solid, melting at about 80°, and decomposed by heating with sodium with formation of a white solid different in smell and melting point from the original solid (see *Montgolfier*, "Action of Sodium on C₁₀H₁₆Cl₂ and C₁₀H₁₅Cl," *Ann. Chim. Phys.*, **14**, 5).

12. When sage camphor was oxidised by long-continued boiling

with 2 : 1 nitric acid it yielded optically inactive camphoric acid, melting at 186° .

13. Carbonic anhydride was found to react on sage camphor, dissolved in toluene, in presence of sodium with production of a solid melting at $199-200^{\circ}$, possessing the properties of camphol, and being optically inactive: the liquid separated from this camphol when neutralised with hydrochloric acid yielded a small quantity of a nearly colourless solid, melting at above 100° , slightly soluble in water, and giving in aqueous solution a white precipitate with lead acetate, therefore most probably consisting of camphocarbonic acid.

The melting and boiling points of sage camphor, the action of nitric acid, of phosphorus pentachloride and pentasulphide (formerly shown to result in production of cymene), and the action of carbonic anhydride in presence of sodium, all point to the inference that this camphor is "chemically identical" with laurel camphor. The optical behaviour of solutions of these compounds is different; but this is probably connected more with the grouping of molecules than with the structure of the molecules themselves.

14. It has been already stated that the samples of oil distilled from the leaves of the common English sage all contained as main constituent a hydrocarbon of the formula $C_{15}H_{24}$, isomeric or identical with cedrene from cedar oil (Gladstone, this Journal [2], 10, 1).

The boiling point of sage cedrene after repeated distillation is about 260° (in a former paper it was given as $264-271^{\circ}$, but this is certainly too high).

The colour of the cedrene from the second sample of English-distilled oil was of a yellower shade of green than that from the earlier sample, the value obtained for the refractive index for mean rays of each oil was, however, the same; the boiling points were also identical.

The cedrene from the last sample of German oil with which I have worked was of dark emerald-green colour, resembling that of the same hydrocarbon from the earlier sample of English oil. The specific gravity, &c., are detailed in the Appendix.

Sage cedrene is almost certainly optically inactive (this Journal, 1878, *Proc.*, p. 298). Sulphuric acid (4 : 1) resinised sage cedrene, even when surrounded by a freezing mixture. About one-fourth of the total quantity was obtained seemingly unchanged by steam distillation.

Hydrochloric acid gas acted on sage cedrene dissolved in ether with production of a purple-coloured oil, which was slowly decomposed on distillation in steam with reproduction of about 25 per cent. of the original cedrene, and a considerable quantity of resin.

Summary.

1. The composition of essential oil of sage varies with the age of the oil. Soon after distillation the oil contains comparatively small quantities of salviol, camphor, and cedrene; the quantities of these—especially of the two former—increase as the oil ages. Probably salviol is first produced by oxidation of the $C_{10}H_{16}$ compound present, and camphor is the product of the further oxidation of salviol.

Oil of sage distilled from the leaves of the English plant is characterised by the presence of much cedrene, boiling at about 260° , with very little $C_{10}H_{16}$ hydrocarbons, and only traces of oxidised compounds.

2. The terpene of sage oil is almost certainly identical with that from French turpentine. The existence in sage oil of an isomeride of terpene, boiling at about 171° , is probable, but cannot yet be regarded as finally determined.

3. Salviol has the formula $C_{10}H_{18}O$, and not $C_{10}H_{16}O$, as formerly supposed; on oxidation with chromic liquor or dilute nitric acid, it yields camphor, melting at 174° , as also oxalic and acetic acids.

4. Salviol is very slightly decomposed on distillation, with production of water, and a $C_{10}H_{16}$ compound or compounds, which is at the same time very slightly polymerised.

The prolonged action of sunlight in presence of air on the $C_{10}H_{16}$ compounds of sage oil probably results in the production of salviol, and if the time be very long, of small quantities of camphor. The prolonged action of light on salviol certainly causes the formation of camphor.

5. The action of phosphoric anhydride on salviol is very complex; the main resultants appear to be polymerides of $C_{10}H_{16}$, a hydrocarbon of this formula boiling at about 171° , a hydrocarbon of the benzene series boiling below 130° , and a paraffin-like hydrocarbon boiling between 170° and 180° . Cymene is not found among the products of this action, when the action is continued for some time.

6. The actions of phosphorus pentachloride, and of bromine on salviol, have not been fully studied. The former, which takes place only at temperatures above the ordinary, results in the production of a chlorinated derivative, which is decomposed on distillation, with formation of a $C_{10}H_{16}$ hydrocarbon, boiling above 157° , and probably accompanied by the same paraffin-like compound, which is one of the products of the action of phosphoric anhydride on salviol.

Salviol is very energetically attacked by bromine, with elimination of much hydrogen, and setting free of carbon; a brominated oil may, however, be separated, and, under special conditions, small quantities of camphor, melting at 174° , are produced.

7. Camphor separates chiefly from those portions of sage oil which

distil from 205—208°. This camphor is partially soluble in salviol, but, if the solution be concentrated, separates therefrom at about -15°. Sage camphor melts at 174°, and boils at 205° (uncorr.). In its reactions with phosphorus pentachloride and nitric acid, and in the fact that camphoric acid, melting at 186°, is obtained by its oxidation, sage camphor appears to be chemically identical with laurel camphor. Sage camphor, as also the camphoric acid obtained from it, is, however, optically inactive.

Sage camphor yields a camphol, melting at 199—200° (and most probably a camphocarbonic acid), when submitted to the action of carbonic anhydride in presence of sodium. The camphol thus obtained is optically inactive.

8. Sage cedrene, boiling about 260°, has been only very partially examined. About 80 per cent. is resinised (polymerised?) by 4 : 1 sulphuric acid, whilst hydrochloric acid appears to form a hydrochloride, which is almost entirely decomposed by steam distillation, with the re-formation of about 25 per cent. of the original cedrene.

9. The compounds present in sage oil are fairly stable when pure, but when mixed even with small quantities of other bodies, they undergo cycles of chemical change. Processes of oxidation, deoxidation, and polymerisation, most probably occur simultaneously during the ageing, and also during the fractionation of sage oil.