XV.—*On the Constitution of Oil of Cajeput.* By MAXIMILIAN SCHMIDL, Assistant to Professor ANDERSON in the Laboratory of Glasgow College.

(Read 17th April 1860.)

The constitution and properties of the essential oils attracted considerable attention during the earlier period of the investigations in organic chemistry, and several of them have contributed in no small degree to the development of the general doctrines of that department of the science. A majority of these substances, however, may be said to be still almost unknown, all the information we possess regarding them being restricted to a single analysis, made on what was obviously a mixture, or to a few observations of a general and often indefinite character. The complex nature of many essential oils, and the want of experience and easy processes for the separation of their constituents, have hitherto deterred chemists from attempting their minute examination, but the progress of the science has increased our knowledge of the methods of investigating these substances, and renders it important that their true constitution and position in the chemical system be definitely fixed. With this object I have taken up the investigation of Oil of Cajeput; our information regarding which is confined to a single analysis made by BLANCHET and SELL, some five and twenty years ago.

Oil of Cajeput is prepared in the East Indies, by distilling along with water the leaves of *Melaleuca Leucadendron*; it was formerly used to a great extent as an external and even internal medicine, but has now become more or less obsolete, and is seldom met with in a pure or unchanged state, except in the hands of wholesale druggists. As introduced into Europe, it possesses a light-green colour resembling a dilute solution of chloride of chromium, which is caused by a resinous colouring matter dissolved in it, but in so small a proportion, that I have hitherto failed to obtain it in sufficient quantity and pure enough for elementary analysis. I suspected, in common with other observers, that this coloration might be due to a salt of copper; but although I always detected this metal in the crude oil, by treating it with nitric acid, when, after its total destruction, the blue nitrate of copper was left behind, or by the still simpler process of passing sulphuretted hydrogen through the oil, when a black precipitate of sulphuret of copper was immediately formed; I nevertheless satisfied myself that it possessed a green colour of its own; since, after the removal of the sulphuret of copper, it exhibited the same appearance, and, on distillation, the latter fractions which passed over had a decided green colour, which could not be due to any salt of copper, as none of its compounds volatilise at the temperature at which these fractions distilled; nor

could I then by any reagent or operation detect the presence of copper, as I did in the crude oil.

The fact, however, that copper almost invariably is found in the crude commercial article, can only be accounted for, either by the use of a copper head in the distilling apparatus of the Indians, or by intentional adulteration employed in order to preserve the green colour of the oil, which it otherwise, as I have convinced myself, loses when in process of time oxidation takes place, in consequence of which a reddish brown colour is produced, which is said to make the article, for medicinal purposes, less saleable.

The Specific Gravity of the Crude Oil at 10° C. = 0.926.—It does not solidify at -25° C.; its taste is pungent and aromatic; its smell only pleasant when diluted, but very disagreeable when concentrated; it is soluble in all proportions in alcohol and ether. When submitted to distillation, it becomes turbid at 120° C., and acquires a yellowish brown colour; at 175° C., it commences to distil over, and before the thermometer indicates 178° , nearly two-thirds of the oil have passed over, the fluid collected being limpid and perfectly colourless; from 178° to 250° C. the mercury rises gradually, without showing any distinct boiling points. The fluid passing over between this long interval changes gradually from a pale yellowish colour into darker shades, approaching always more and more to green, until at last the fraction between 240° to 250° C. becomes of a dark untransparent green colour.

At 265° C. the retort is almost dry, retaining some metallic copper mixed with carbonaceous and resinous matter, which, when treated with ether, imparts to this reagent a green colour, and on evaporation of the latter a green resin is left behind, which is soluble in the rectified fraction (boiling at 175° C.), and thereby able to restore the coloured appearance of the original oil.

Whether the fractions beyond 178° C. be special and pre-existing constituents of the crude oil, or mere products of decomposition, and therefore of changeable character, I am as yet not able to state, since the results of operations performed with them are either contradictory as to this effect, or not yet sufficient to countenance the one or the other of these opinions; but still, in the course of time, and in a second paper, I hope I will be able to give some satisfactory accounts about them.

Most of my operations are therefore confined to the first large fraction, boiling at 175° to 178° C.; in particular cases, however, which I shall endeavour to specify, the crude oil has been employed.

I. BIHYDRATE OF CAJPUTENE, $C_{20}H_{16} + 2HO$.

I commenced my experiments by agitating the rectified fraction with bisulphate of soda, by means of which I satisfied myself of the absence of aldehydes and other bodies, capable of combining with that substance. And as, from the

fixed boiling point, there could be no doubt that this fraction consisted only of one substance, I at once proceeded to its elementary analysis, after having had it rectified four times, and well dried over chloride of calcium. The following are the detailed results:—

(a)	2.60 grains of substance gave	.	.	.	7.42 CO_2	2.79 HO.
(b)	3.29 ,, ,,	.	.	.	9.22 CO_2	3.48 HO.
				A.	B.	
Carbon,	.	.	.	77.83	77.86	77.92
Hydrogen,	.	.	.	11.92	11.91	11.68
Oxygen,	.	.	.	10.25	10.23	10.40
				100.00	100.00	100.00
						} Theory.

These results agree with those of Messrs BLANCHET and SELL,* who found Oil of Cajeput to consist of 77.92 carbon, 11.69 hydrogen, and 10.39 oxygen, to which they applied the name of Hydrate of Dadyl.

In order, therefore, to fix its rational formula, I then proceeded to determine its vapour density, of which the following are the details:—

Temperature of air,	.	.	.	14° C.
Temperature of vapour,	.	.	.	85° C.
Excess of weight of balloon,	.	.	.	0.580 grm.
Capacity of balloon,	.	.	.	200.00 C.C.
Residual air,	.	.	.	...
Density of vapour	.	.	.	5.43

The formula $\text{C}_{20} \text{H}_{16} 2\text{HO}$ requires—

20 volumes of carbon,	.	.	.	.	20 × 0.831	= 16.620
18 ,, hydrogen,	.	.	.	.	36 × 0.0693	= 2.490
2 ,, oxygen,	.	.	.	.	2 × 1.050	= 2.100
						21.21

21.21 : 4 = 5.30 theoretical result.

From the close agreement of the experiment with the theory, I could not hesitate to represent Oil of Cajeput by the formula $\text{C}_{20} \text{H}_{18} \text{O}_2$; and, induced by reactions of the substance, to be mentioned hereafter, I assigned to it the name of Bihydrate of Cajputene,† thereby indicating its resemblance with Oil of Turpentine, in comparison with which it possesses (besides $\text{C}_{20} \text{H}_{16}$) two additional equivalents of water.

Physical and Chemical Qualities and Reactions of Bihydrate of Cajputene.

The specific gravity of this substance at 17° C. is = 0.903; it boils constantly at 175° C., and is soluble in all proportions in oil of turpentine, alcohol, and ether.

* *Annalen der Pharmacie*, vii. 162.

† In order to avoid long words I write Cajputene and not Cajeputene, thus rendering the “j” half mute like “i.”

When exposed in a moist state for a considerable time to atmospheric air, it changes into a reddish fluid, showing at last a pretty strong acid reaction to litmus paper.

In contact with an aqueous solution of potash a soluble salt is formed, the acid of which is precipitated by hydrochloric or sulphuric acid as a resinous substance.

When dropped into melted potash, a compound is formed which is soluble in water and decomposed by a strong inorganic acid; the precipitate being also a resin.

When treated at high temperature with sodium, a crystalline mass is produced, which is soluble in water and alcohol, and consists of soda and an organic substance; the latter being likewise separable by strong acids (organic and inorganic), as a resin of a very agreeable smell.

If the vapours of the oil be passed through a combustion tube filled with soda-lime and maintained at a red heat, an oily product is formed, which is obtained in a receiver suitably connected with the tube. This product possesses a peculiar smell, entirely different from that of the original substance, and a bright yellow colour; the soda-lime itself is thoroughly blackened with charcoal, and on the addition of an acid, it evolves copiously carbonic acid, thereby indicating that some decomposition must have taken place in the oil when passing through the tube; the analyses of the changed product will follow afterwards.

Bihydrate of cajputene does not seem to be changed when digested with peroxide of lead.

If the oil be distilled over permanganate or bichromate of potash in the presence of dilute sulphuric acid, a thick resinous fluid is produced.

Fuming nitric acid acts very violently on the oil, red fumes of nitrous acid being evolved even in the cold, and an abundance of oxalic acid being formed. Commercial nitric acid produces the same effect at boiling temperature; at ordinary temperature, however, it acts slowly, converting the oil into a thick red fluid.

Fuming sulphuric acid entirely changes the molecular condition of the oil, even if the latter be kept during the operation immersed in ice, a thick brown fluid being formed, which boils beyond 360° C.

Commercial sulphuric acid acts at low temperature very slowly on the oil, so, that after four or five hours little or no change is observed if the acid be removed and the oil well washed; but if the temperature be allowed to rise, either by artificially employed heat, or by continued unchecked chemical action, sulphurous acid is given off, blackening of the oil commences, and may even go on to total destruction of the substance. This can be avoided by caution, and then a sulpho-compound will be formed, which gives with baryta a soluble salt.

Dilute sulphuric acid acts most curiously on the oil, since, in the opposite manner to the fuming and commercial acid, it not only does not deprive the oil of its two equivalents of water, but causes the formation of a crystalline substance which possesses four equivalents of water in addition to the two original ones.

Anhydrous phosphoric acid deprives the oil of its two equivalents of water, when heated along with it.

Chloride of zinc, under similar circumstances, does not act so energetically, the two equivalents of water having been found to have been only partly removed from the oil after the application of that reagent.

Commercial hydrochloric acid, if left in contact for some weeks with the crude oil, produces a crystalline compound. Gaseous hydrochloric acid produces, under particular circumstances to be mentioned below, two kinds of crystalline compounds.

Chlorine, when passed through the oil, raises its temperature to a considerable height, producing, however, no visible change in it.

Iodine dissolves in the oil, and, under precautions which will be further described, different crystalline compounds may be formed.

Bromine acts very briskly, and produces under similar circumstances, like iodine, crystalline compounds.

Before leaving the Bihydrate of Cajputene, I will briefly note the results of the analyses performed with that secondary product, which was obtained when the first large fraction had been passed through red-hot soda-lime.

Fraction 180° to 185° C.

(a)	2.49 grains of substance gave,	.	.	.	7.29 CO ₂	4.25 HO.
(b)	4.15 " "	.	.	.	12.18 CO ₂	4.51 HO.
						A. B.
					79.76	80.03
Carbon,					12.20	12.07
Hydrogen,					8.04	7.90
Oxygen,					100.00	100.00

The increase of carbon and hydrogen shown by these analyses on the one hand, and the presence of a large amount of charry matter and carbonic acid in the employed soda-lime on the other, indicate sufficiently that by that operation some change or another must have taken place in the oil; but as I have not yet entered upon any investigation of this product, further than the above analyses, I refrain from giving any other opinion about it, except that the above results would best correspond with the empirical formula C₂₆ H₂₄ O₂₀, the percentages of which are—

79.59 C.
12.44 H.
7.97 O.
100.00

Since I succeeded in obtaining a crystalline iodine compound, and a hydrate of

this secondary product, I hope to be able to give some further and more satisfactory results about it in a subsequent paper.

II. MONOHYDRATE OF CAJPUTENE.— $C_{20}H_{16} + HO$.*

The crude oil is raised to its boiling point in a deep open vessel, and when commercial sulphuric acid is continuously dropped into it, violent ebullition—which after a short time is accompanied by a peculiar crackling sound—takes place. As soon as this is observed the flame is lowered, and the acid very cautiously added, until almost suddenly the fluid assumes a dark colour, which goes on in one moment from the surface throughout its whole depth. Should this be overlooked, and the acid indiscriminately added, the process goes on further than desired, sulphurous acid is formed, both equivalents of water removed, and the products become very complicated. At the moment, therefore, when the darkening of the substance just commences, the vessel must be removed from above the flame and allowed to cool. The upper oily fluid is then separated from the acid, well washed and distilled. Amongst the fractions obtained thereby, I chose that which passed over at 170° to 175° C., as having been the largest; and after several rectifications, I proceeded to ascertain its composition, and to determine the density of its vapour, of which the following are the details:—

(a)	3.75 grains of substance gave,	.	.	11.38 CO_2	4.00 HO.
(b)	3.45 „ „	.	.	10.47 CO_2	3.59 HO.
(c)	2.04 „ „	.	.	6.18 CO_2	2.180 HO.
Carbon,	.	82.73	82.79	82.62	82.75
Hydrogen,	.	11.85	11.59	11.87	11.72
Oxygen,	.	5.42	5.62	5.51	5.53
		<hr/>	<hr/>	<hr/>	<hr/>
		100.00	100.00	100.00	100.00

Vapour Density.

(1.)	(2.)	(3.)
Temperature of air, 18° C.	Temperature of air, 10° C.	Temperature of air, 20° C.
Temperature of vapour, 220° C.	Temperature of vapour, 210° C.	Temperature of vapour, 200° C.
Excess of weight, 0.404 gm.	Excess, 0.405 gm.	Excess, 0.520 gm.
Capacity, 159.5 CC.	Capacity, 158.4 CC.	Capacity, 214 CC.
Residual air	Residual air, 2 CC.	Residual air, 14. CC.
		Barometer, 750 M.M.
D = 5.19.	D = 5.26.	D = 5.27.

* Since April last, the time when the present paper was read before the Royal Society, I undertook, at the suggestion of several professional friends, to prepare anew the substances under consideration. The results arrived at now, by repeated combustions and determinations of its vapour density, showing nowhere a difference of much more than one-tenth, if compared respectively with one another, or with those obtained previously, leave really little or no doubt at all about the purity and chemical unity of the substance—however novel, singular, and exceptional it may seem, that the vapour of a body containing one atom of oxygen should condense to four volumes. However, as the substance is easily prepared, the experiment should be repeated by others, and not only with Oil of Cajepu, but with all the bihydrates of the turpentine-radical. Like experiments with bodies of ana-

The formula, $C_{29}H_{17}O$, requires—

20 volumes of carbon	=	20×0.831	=	16.620
17 „ hydrogen	=	34×0.0693	=	2.356
1 „ oxygen	=	1×1.108	=	1.108
				20.090

$$20.09 : 4 = 5.02.$$

III.—CAJPUTENE, ISOCAJPUTENE, PARACAJPUTENE— $C_{20}H_{16}$.

The rectified oil is allowed to cohobate over anhydrous phosphoric acid for about half an hour ; on entire distilling, an oil passes over, which by repeated rectification separates into three principal fractions of distinct and steady boiling points.

Cajputene is one and the first of these fractions ; it passes over at 160° to 165° C. It is perfectly colourless, and possesses a very pleasant smell, resembling that of hyacinths ; it is insoluble in alcohol, soluble in ether and oil of turpentine ; its specific gravity at 15° C. = 0.850.

The following are the details of its analysis :—

(a)	3.20 grains of substance gave	10.36 CO ₂	3.43 HO.	
(b)	3.90 „ „	12.63 CO ₂	4.10 HO.	
Carbon,	. . .	88.29 } <i>a</i>	88.34 } <i>b</i>	88.24 } Theory.
Hydrogen,	. . .	11.91 }	11.78 }	11.76 }
		<hr/> 100.20	<hr/> 100.12	<hr/> 100.00

Vapour Density.

Temperature of air,		16° C.
Temperature of vapour,		204° C.
Excess of balloon,		0.399 gm.
Capacity of balloon,		165 CC.
Residual air,		7 CC.

$$D = 4.717.$$

The formula requires .465.

Reactions.

If Cajputene is exposed to a current of gaseous hydrochloric acid, a beautiful violet fluid is produced ; but no crystalline compound is deposited, even if the oil be maintained during the operation at -10° C, and preserved afterwards for any length of time. A mixture of commercial nitric and sulphuric acid acts very vio-

luous composition will probably increase the number of similar instances. Further remarks as to its reactions, physical qualities, secondary products, and its relation to the Bihydrate of Cajputene, compared with which it might prove to be an analogous ether, I will endeavour to give in a subsequent paper.

lently on Cajputene, producing a yellow brittle resin. Bromine, also, acts very briskly in contact with it, producing a dark viscid oil. Iodine behaves indifferently at ordinary temperature towards it; but at a raised temperature hydrogen is copiously evolved, and a black fluid produced. Cajputene resists the influence of atmospheric air, retaining its peculiar smell and colourless appearance even after a very long exposure to this generally powerful agent.

Isocajputene is the second fraction, separated from that oily product obtained by the action of anhydrous phosphoric acid; it passes over at 176° C. to 178° ; its specific gravity at 16° C. is = 0.857; it is insoluble in alcohol, and mixes in all proportions with ether and with oil of turpentine; its smell is different from and less agreeable than that of Cajputene, and when exposed to atmospheric air it soon acquires a yellow colour, and a more pungent aromatic smell.

The same body may be procured by continued action, at a raised temperature, of commercial sulphuric acid upon the Bihydrate of Cajputene, especially if the oil be distilled along with the acid.

The following are the details of the analyses performed:—

(1.) *Product got by the Action of Phosphoric Acid.*

(a)	2.24 grains of substance	gave	7.24 CO ₂	2.35 HO.	
(b)	2.70	" "	8.72 CO ₂	2.84 HO.	
Carbon,	.	.	88.16 } ^a	88.18 } ^b	88.24 } Theory.
Hydrogen,	.	.	11.64 }	11.68 }	11.76 }
			<hr/> 99.80	<hr/> 99.86	<hr/> 100.00

(2.) *Product got by the Action of Sulphuric Acid.*

(a)	4.20 grains of substance	gave	13.56 CO ₂	4.50 HO.	
(b)	2.93	" "	9.48 CO ₂	3.12 HO.	
Carbon,	.	.	88.05 } ^a	88.23 } ^b	
Hydrogen,	.	.	11.90 }	11.83 }	
			<hr/> 99.95	<hr/> 100.06	

Vapour density of (1.) = 4.82; of (2.) = 4.52; theory = 4.65.

Nitro-sulphuric acid, gaseous hydrochloric acid, bromine, and iodine react in the same way on Isocajputene as on Cajputene. Commercial and even dilute sulphuric acid, dilute nitric, and dilute hydrochloric acid, all of which behave indifferently towards Cajputene, react upon Isocajputene, producing by mere contact, in a very short time, dark viscid fluids.

Paracajputene, C₄₀ H₈₂, is the last fraction of those isomeric hydrocarbons produced by the action of anhydrous phosphoric acid; it distils at 310° to 316° C.; is very viscous, and of lemon-yellow colour, but if looked at in certain directions, it shows a beautiful deep blue fluorescence. It is insoluble in alcohol and oil of turpen-

tine, but soluble in ether, and when exposed to atmospheric air, it rapidly oxidises, acquiring a red colour and resinous consistence.

Analyses.

(a)	4.19 grains of substance	gave 13.57 CO ₂	4.55 HO.
(b)	3.15	„ „ 10.19 CO ₂	3.42 HO.
Carbon		88.33	} ^a 88.28
Hydrogen		12.06	
		<hr/>	<hr/>
		100.39	100.34

Vapour Density.

Temperature of air,		16° C.
Temperature of vapour,		320° C.
Excess of weight of balloon,		0.599 gm.
Capacity of balloon,		198 CC.
Residual air,		22 CC.

$$D = 599 + \left(\frac{198 \times 0.0001224}{176 \times 0.000605} \right) = \frac{84135}{10168} = 7.96.$$

The theory requires double the quantity of what is required for the formula $C_{20}H_{16} = 4.65 \times 2 = 9.30$. The great difference between the experimental and theoretical results can only be accounted for by the high boiling point of the substance, and its great tendency to decompose at that temperature.

Reactions.

Gaseous hydrochloric acid produces a dark violet fluid, which does not deposit any crystalline compound, even if the operation be performed at -10° C. Nitro-sulphuric acid does not act so violently as on the two foregoing fractions.

IV. HEXHYDRATE OF CAJPUTENE, $C_{20}H_{16} + 6 HO$.

Two parts of dilute sulphuric acid are added to one of the crude Oil of Cajepu; the mixture is then well shaken for several days, until the watery layer acquires a yellowish colour; thereby the presence of organic matter in the latter is indicated. After that the mixture is left to itself, when, usually from about the tenth day and upwards, crystalline tufts, adhering to the sides of the vessel, are found.

These crystals are sparingly soluble in cold, but readily in boiling alcohol; they fuse at 120° C., and solidify again at 85° C. When submitted to dry distillation, the oily fluid which passes over solidifies again in the colder parts of the receiver; but from the limited amount of substance then at my disposal, I could not ascertain if this product of sublimation was of the same or of altered composition.

The following are the detailed results of the analyses performed with the substance after previous recrystallisation out of alcohol:—

(a)	2.65	grains of substance	gave	6.17	CO ₂	2.86	HO.	
(b)	2.61	"	"	6.04	CO ₂	2.61	HO.	
(c)	2.98	"	"	6.90	CO ₂	3.21	HO.	
Carbon,	63.39	} a	63.11	} b	63.11	} c	63.15	} Theory.
Hydrogen,	11.99		11.96		11.92		11.57	
Oxygen,	24.62		24.93		24.97		25.28	
	<hr/> 100.00		<hr/> 100.00		<hr/> 100.00		<hr/> 100.00	

Crystals of the same composition I found deposited in a secondary fraction of the crude oil, which on distillation passed over at 210°–230° C., and was left for a very long time moist and exposed to the action of atmospheric air. When the crude oil is mixed with dilute nitric acid and alcohol in the same proportions as are used when a similar compound is contended for in oil of turpentine, no crystals are found before at least seven or eight months; after the lapse of this time, however, such appear and are seen suspended in the oil, which meanwhile changes into a heavy black fluid. The quantity which I got by this method was so small, that I was not able to carry out any operations with it in order to satisfy myself if its composition and qualities really were the same with, or different from, the above-mentioned Hexhydrate of Cajputene; but as I am again preparing the same substance just now, I hope to give some account of it in a second paper. There also I intend to describe other crystalline compounds which I just recently obtained, by the action of dilute nitric acid upon the total crude oil, upon the rectified fraction, boiling at 175° C., upon the second fraction, boiling from 178°–200° C., and upon the last green fraction, boiling from 200°–255° C. By the comparison of these crystalline substances I may perhaps become enabled to state something more satisfactory about the nature of those secondary fractions of the crude oil.

V. HYDROCHLORO COMPOUNDS OF CAJPUTENE.—*Bi*hydrochlorate of Cajputene, C₂₀H₁₆ + 2 HCl.

If gaseous hydrochloric acid be passed through the rectified oil, which is maintained at low temperature, a violet fluid is produced, which, after 10–15 minutes, suddenly solidifies into a crystalline mass, so that the orifice of the delivery-tube becomes obstructed, thereby preventing the further application of the gaseous acid. This crystalline compound, however, I was unable to analyse, since no sooner was it removed from the vessel where prepared than it deliquesced, even when pressed between blotting paper, which by means of artificial cold had been maintained at –25° C.; the fluid, also, resulting from that deliquescent substance, gave off constantly fumes of hydrochloric acid, and on distillation it decomposed entirely, showing no constant boiling point. If, however, immediately after the application of gaseous hydrochloric acid, that crystalline mass be thrown

into a vessel containing water or alcohol, beautiful long prisms are formed after a few days, which contain no chlorine, and seem to be of the same composition as the Hexhydrate of Cajputene.

If the oil be mixed with a third of its volume of alcohol, or if, in place of alcohol, strong aqueous hydrochloric acid be taken, and gaseous hydrochloric acid then passed through either of the mixtures, a crystalline compound is formed which is of steady constitution, and different in all its physical and chemical qualities from the one formed without the presence of alcohol or aqueous hydrochloric acid.

The following are the detailed results of its elementary analyses :—

(a)	0.266	gram. of substance	gave	0.562	CO ₂	0.214	HO.
(b)	0.268	"	"	0.565	CO ₂	0.216	HO.
(c)	0.145	"	"	0.205	AgCl.		

Carbon,	57.61	} <i>a</i>	57.54	} <i>b</i>	} <i>c</i>	57.41	} Theory.
Hydrogen,	8.93		8.95			8.61	
Chlorine,	.		.			34.49	
						<hr/> 100.00	

Bihydrochlorate of Cajputene melts at 55° C., and solidifies again at about 30° C.; when submitted to dry distillation, it gives off fumes of hydrochloric acid at 60° C., and splits into several fractions, one of which is of constant boiling point and steady chemical composition, which will be mentioned afterwards. When boiled with an alcoholic or aqueous solution of potash it undergoes no change, unless a high temperature be maintained for a long time by cohobation, when one equivalent of hydrochloric acid is removed. It is sparingly soluble in cold, but readily soluble in boiling alcohol and in ether; it possesses no taste or smell whatever, and differs in that and in most of its other physical and chemical qualities from the isomeric compound in oil of turpentine, called the artificial camphor; out of alcohol it crystallizes in beautiful radiating tufts.

VI. MONOHYDROCHLORATE OF CAJPUTENE, $C_{20}H_{16} + HCl$.

When the Bihydrochlorate of Cajputene is submitted to distillation, amongst several other fractions, one passes over which has been mentioned before as possessing a constant boiling point. This fraction distils at 160° , and its analyses gave the following results :—

(a) 0·330	gram.	of substance	gave	0·848 CO ₂	0·295 HO.			
(b) 0·257	"	"		0·654 CO ₂	0·233 HO.			
(c) 0·172	"	"		0·143 chloride of silver.				
Carbon,	.	70·00	} <i>a</i>	69·40	} <i>b</i>	}	69·76	} Theory.
Hydrogen,	.	9·93		10·07			9·88	
Chlorine,	.	.		.			20·53	
						} <i>c</i>		
							}	
							100·00	

A product of similar composition is obtained when the Bihydrochlorate of Cajputene is treated for several days at high temperature with an aqueous or alcoholic solution of potash; the smell of this substance, however, is so entirely different from that of the other monohydrochlorate (reminding of pelargonic ether), that some further investigation may probably lead to more striking chemical as well as physical differences between these two isomeric substances.

VII. BICHLORIDE OF CAJPUTENE, $C_{20}H_{16} + 2Cl$.

The large rectified fraction of Oil of Cajeput is mixed with some very dilute nitric acid, and then exposed to a stream of gaseous hydrochloric acid, when, after a few minutes, violent evolution of yellow and red fumes, consisting of chlorine and nitrous acid, takes place. The gaseous hydrochloric acid is allowed to pass so long till the oily fluid in the vessel has entirely sunk to the bottom, having then the watery layer (reversely to the beginning of the operation) above itself.

If the vessel be, after the operation, kept at a low temperature, a crystalline compound may be formed, which, however, I was only once fortunate enough to obtain, but in so small a quantity that I could not make more than one analysis of it, by means of which, however, I convinced myself of the presence of chlorine in that substance. In ordinary cases, therefore, I had to content myself with a limpid brown fluid, which, in consequence of the adhering nitric and nitrous acid, I redistilled over a strong solution of potash; and thus prepared I submitted it to its elementary analyses, of which the following are the detailed results:—

(a)	2.87	grains of substance	gave	6.05	CO ₂	2.09	HO.
(b)	3.61	„	„	7.60	CO ₂	2.63	HO.
(c)	2.91	„	„	4.10	chloride of silver.		
(d)	4.84	„	„	3.97	„		

Carbon,	.	57.49	} a	57.41	} b					57.98	
Hydrogen,	.	8.09		8.09						7.72	
Chlorine,	.	.	.	.	34.57	} c	34.21	} d		34.30	} Theory.
										<hr/>	
										100.00	

As this substance could not be distilled by itself without decomposition unless in vacuo, I was not able to take its vapour density. It possesses an extremely fine and agreeable smell, and may be kept for any length of time without undergoing any decomposition. When boiled with nitrate of silver, a peculiar detonation takes place, and chloride of silver is formed.

Before leaving the compounds which are produced by the action of hydro-

chloric acid, I must observe that only recently I got another crystalline compound which had been formed by the mere contact of the crude oil with commercial hydrochloric acid, which, however, I have not yet analysed, and must therefore preserve for a following paper.

BROMO COMPOUNDS.

VIII. TETRABROMIDE OF CAJPUTENE, $C_{20}H_{16} + 4 Br$.

When the rectified oil is shaken with bromine water, a red resin is formed, out of which a solid substance crystallizes in small white prisms. This crystalline compound, however, is unmanageable, in consequence of the readiness with which it deliquesces and decomposes. When dry bromine is dropped into the oil a very brisk action takes place, and the sides of the vessel become covered with yellow needles, but which immediately disappear again; if bromine be added so long till almost no reaction is observed in the fluid, a dark, thick, and viscous oil is produced, which, after the lapse of several weeks, deposits a granular substance. As soon as this is observed, alcohol is added to the whole mixture, and boiled along with it. By this operation the granular substance is extracted, and a heavy oil left behind. On the cooling of the alcohol a soft crystalline substance is deposited, of a fatty lustre, resembling very much cholesterine when crystallizing out of the same menstruum. The following are the details of its analyses:—

(a)	2.60	grains of substance gave	2.51	CO ₂	0.994	HO.
(b)	3.21	„ „	3.05	CO ₂	1.20	HO.
(c)	3.27	„ „	5.38	bromide of silver.		
Carbon,	. 26.32	} <i>a</i>	25.97	} <i>b</i>	. . .	26.31
Hydrogen,	. 4.24		4.15		. . .	3.52
Bromine,	. . .		. . .		. 70.03 ;	70.17
					<hr/>	100.00

} Theory.

} Theory.

This substance is soluble in ether and boiling alcohol; it melts at 60° C., and solidifies again at 32° C. When submitted to dry distillation, the fluid which passes over crystallizes again in the cooler parts of the retort; whether this product is changed or not I have not yet ascertained. When boiled with a solution of caustic potash, the tetrabromide seems to remain unaltered.

Another crystallized bromine compound has been obtained by the action of phosphorus, dissolved in bisulphide of carbon, on the oil dissolved along with bromine in the same menstruum; the substance, however, at my disposal was so limited in quantity as to preclude the possibility of a satisfactory analysis.

IODINE COMPOUNDS.

XI. HYDRIODATE OF HYDRATE OF CAJPUTENE, $C_{20}H_{16} + HO + HI$.

If iodine be added in small quantities to the crude or rectified oil, no reaction seems to take place; if, however, the fluid be heated, such is observed, as the oil, under the evolution of fumes of hydriodic acid, changes into a black heavy fluid; but in order to get a crystalline compound, no artificial heat in this way is allowed to be applied, as by its application the action of the iodine goes too far, resulting in a viscous substance, out of which nothing can be made. After the addition of the iodine the fluid must be stirred rather constantly, and the heat thus produced by the friction of the rod, as well as the mechanical distribution of the iodine, favour the action between the two substances, so that after a few minutes the temperature of the fluid rises from 10° to 40° C. When this is observed, no more iodine is to be added, and the whole vessel is immersed in cold water, when, after a very short time, a black crystalline compound is deposited in the bottom of it. After the oily fluid is filtered off, the solid substance is pressed between blotting paper, and, when nearly dry, dissolved in alcohol or ether, out of which it crystallizes in prisms of beautiful yellow-green metallic lustre.

The following are the results of some of the analyses performed with it:—

	(a)	3.63 grains of substance gave	5.71 CO ₂	2.30 HO.							
	(b)	3.26 " "	5.18 CO ₂	1.97 HO.							
	(c)	2.69 " "	4.28 CO ₂	1.69 HO.							
	(d)	5.55 " "	4.78 iodide of silver.								
Carbon,	42.91	} a	43.33	} b	43.21	} c	.	.	.	43.95	} Theory.
Hydrogen,	7.01		6.71		6.98		.	.	.	6.59	
Oxygen,	.	.	.	.	.	.	.	.	2.94		
Iodine,	.	.	.	.	.	.	.	46.51 d	46.52		
									100.00		

This compound is very soluble in alcohol and ether, insoluble in water, in contact with which it does not become decomposed. It is, however, a very unstable substance, as it easily deliquesces in the course of time, and when melted, which it does at 80° C., it is not recrystallizable. In contact with a cold solution of potash it soon assumes a fluid condition, losing some of its iodine, which at a raised temperature it gives off entirely.

X. HYDRIODATE OF CAJPUTENE, $C_{20}H_{16} + HI$.

A solution of phosphorus in bisulphide of carbon is added to a solution of iodine and oil of Cajeput in the same menstruum. As soon as this is done, a very brisk reaction takes place; the vessel becomes so hot that it cannot be touched by the bare hand of the operator; red oxide of phosphorus is formed

and precipitated; the oily fluid acquires a reddish colour, and gives off fumes which, by the prevalence of the volatile oil, I could not exactly recognise, nor was I, by the peculiarity of the operation, able to receive them under a pneumatic trough. The reaction, however, may be represented by the following simple equation :—

according to which gaseous phosphoretted hydrogen, oxide of phosphorus, and phosphoric acid would be formed; the last two of which I always found present in the fluid out of which the Hydriodate of Cajputene, in the course of ten or twelve days, crystallized. These crystals are deposited in cells like those of beehives, and possess a black metallic lustre. The following are the detailed results of the analyses :—

	(a)	4.39 grains of substance gave	7.29 CO ₂	2.48 HO.		
	(b)	3.01 " "	5.01 CO ₂	1.72 HO.		
	(c)	5.54 " "	5.02 iodide of silver.			
Carbon,		45.29 } ^a	45.36 } ^b	} ^c {	45.45 } Theory.	
Hydrogen,		6.31 }	6.35 }		6.43 }	
Iodine,		.	.		48.85 I }	48.12 }
				<hr/>	100.00	

Hydriodate of Cajputene is soluble in alcohol and ether, and more stable than the preceding iodo-compound, as it remains for any length of time, and even if boiled with a solution of potash, unchanged.

Secondary products of this and the other iodo-compound I intend to describe in a following paper, which I will endeavour to finish as soon as possible.

Finally, I consider it my duty to express my sincerest thanks to Professor Dr Thomas Anderson, who so generously and forbearingly supported me with all kinds of mental and material aid previous to and during the time of this investigation.