XIV.—*Isomeric Terpenes and their Derivatives. Part III. On the Essential Oils of Wormwood and Citronella.*

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LEBLANC has shown that the main constituent of oil of wormwood (*Artemisia Absinthium*, L.) is an isomeride of camphor, boiling at 204° ; to this body the name *absinthol* has been given by Gladstone, who has likewise found in the oil of citronella (*Andropogon Schœnanthus*), a substance of the same composition, to which the name *citronellol* has been applied by him (*Chem. Soc. Journal* [2], x, 7).

Samples of these oils, in what was believed to be a state of purity, were obtained from Dr. Septimus Piesse, and examined with the following results :—

§ 1. *Oil of Wormwood. Proximate Constituents.*

The oil examined began to boil at 200° , and for the most part distilled over below 220° ; the residue left in the retort when distilled, until the boiling-point rose to 300° , yielded at that temperature and upwards a vapour of fine blue tint, condensing to a magnificently blue liquid, the *azulene* of Piesse, and the *cerulene* of Gladstone. A small quantity (about 2 per cent.) of black resin, not volatile at 350° , was left in the retort.

On fractional distillation of the portion coming over below 220° , a small quantity of a terpene, boiling at about 150° , was isolated; this constituted about 1 per cent. of the oil examined. After several distillations over sodium,

0.2220 grm. gave 0.712 CO_2 and 0.243 H_2O .

	Calculated.		Found.
C_{10}	120	88.23	87.47
H_{16}	16	11.77	12.16
$\text{C}_{10}\text{H}_{16}$	136	100.00	

Probably this retained a trace of some oxidised substance; the total quantity was too small for perfect purification.

A yet smaller quantity of hydrocarbon, boiling between 170° and 180° , was also present

The great majority boiled at 200° — 201° (corrected), and gave the following numbers:

0.2345 gram gave 0.672 CO_2 and 0.222 H_2O .

	Calculated.		Found.
C_{10}	120	78.94	78.17
H_{16}	16	10.53	10.52
O	16	10.53	—
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$\text{C}_{10}\text{H}_{16}\text{O}$..	152	100.00	

Hence this substance is isomeric with camphor and with myristicol from nutmeg oil. Unlike the latter, continued distillation does not seem materially to change its composition either in raising its boiling-point or causing decomposition into water and other bodies. When freshly distilled, it is perfectly colourless, but in a few hours it acquires a yellowish tint, even when kept in a tightly stoppered bottle in the dark.

§ 2. Oil of Citronella: proximate Constituents.

On distillation, the greater part of this oil was found to pass over between 195° and 240° ; but the greater part (boiling near 210°) was found to be considerably altered by continued heating, a decomposition being produced, water and substances boiling above 220° being found: after five fractionations about two-fifths of the substance originally used was not volatile below 230° .

The oil employed also contained a soft resinous substance not volatile at 260° , and constituting about 20 per cent. of the oil used.

A. Distillate at 200° — 205° , 0.3025 gram gave 0.858 CO_2 and 0.312 H_2O .

B. Distillate at 210° — 215° , 0.2040 gram gave 0.5815 CO_2 and 0.218 H_2O .

C. Distillate at 215° — 220° , 0.2045 gram gave 0.578 CO_2 and 0.215 H_2O .

D. Distillate at 220° — 225° , 0.2735 gram gave 0.7815 CO_2 and 0.291 H_2O .

	Calculated		Found.			
	For $\text{C}_{10}\text{H}_{16}\text{O}$.	For $\text{C}_{10}\text{H}_{18}\text{O}$.	A.	B.	C.	D.
Carbon. . . .	78.94	77.92	77.36	77.74	77.08	77.93
Hydrogen . .	10.53	11.69	11.46	11.88	11.68	11.82

It hence appears that the main constituent in the distillate B, C, and

D (jointly constituting more than half of the oil used) was a body indicated by the formula $C_{10}H_{18}O$, whilst the few drops obtained boiling at near 200° , contained rather less hydrogen.

On the other hand, Gladstone found the main constituent to be a body boiling tolerably constantly at 199° — 205° , and giving numbers agreeing well with the formula $C_{10}H_{16}O$; it hence seems probable that the composition of oil of citronella (and probably of other essential oils) is not absolutely constant, probably varying with the season, age of plant, &c., &c. That the oxidised body in distillates B, C, and D is really indicated by $C_{10}H_{18}O$ and not by $C_{10}H_{16}O$, is manifest from its reactions (vide *infra*), which are in many respects identical with those undergone by the isomeric substance (boiling at 175° — 178°) found by Schmidl in oil of cajeput (this Journal, xiv, 63).

After several successive heatings, portions of altered substances were left not volatile below 270° : one specimen contained—

Carbon		81.5
Hydrogen		11.1

As the carbon had increased whilst the hydrogen had diminished, probably the elements of water had been partially eliminated; and in this respect therefore the action of heat on the oxidised constituent of citronella oil is different from that on myristic oil, the latter becoming polymerised without losing the elements of water.

§ 3. Action of Zinc Chloride on Absinthol and Citronellol.

A. Pure absinthol was cautiously heated with zinc chloride; a vigorous reaction was evident, and water and a hydrocarbon distilled over: most of the absinthol, however, was converted into a non-volatile resin. The hydrocarbon, after agitation with sulphuric acid and fractional distillation over sodium, boiled almost wholly at 175° — 178° , and gave the following numbers; the yield of pure substance was about 20 per cent. of the absinthol employed.

0.2680 gram gave 0.877 CO_2 and 0.260 H_2O .

		Calculated.	Found.
C_{10}	120	89.55	89.25
H_{14}	14	10.45	10.78
$C_{10}H_{14}$	134	100.00	

B. Citronella distillates B and C were mixed and heated with zinc chloride: much resin was formed, and water and a hydrocarbon distilled over. After treatment with sulphuric acid and distillation over sodium, this boiled between 170° — 180° , and gave the following numbers:

0.2420 gram gave 0.768 CO₂ and 0.279 H₂O.

	Calculated for C ₁₀ H ₁₆ .	Calculated for C ₁₀ H ₁₈ .	Found.
Carbon	88.24	86.96	86.55
Hydrogen	11.76	13.04	12.81

Probably therefore a mixture of hydrocarbons is formed, as is known to be the case when camphor is similarly treated; the main constituent containing much more hydrogen than is present in cymene: the total yield of hydrocarbon was only about 10 per cent. of the substance used.

The resin simultaneously produced contained carbon 85.4, hydrogen 11.7, and was therefore formed by partial removal of the elements of water. Schmidl found that zinc chloride only partially dehydrates the constituent C₁₀H₁₈O contained in oil of cajeput, phosphoric anhydride yielding a mixture of terpenes and polymerides.

§ 4. Action of Phosphorus Pentasulphide on Absinthol and Citronellol.

The yield of hydrocarbon by the action of zinc chloride being but small, the action of phosphorus pentasulphide was examined. Pott has shown that camphor when treated with this substance forms cymene in a state of considerable purity; and Flesch has recently found (*Deut. Chem. Ges. Ber.*, vi, 478) that cymyl-sulphydrate boiling at 235°—236°, is simultaneously produced: in the case of absinthol and citronellol, therefore, cymene and cymyl sulphydrate, and a terpene, might be anticipated as the respective products; and in fact these substances are formed. The majority of the substances used, however, is in each case converted into a resin not volatile at 350°.

A. Absinthol was heated with about its own weight of phosphorus pentasulphide; a tolerably vigorous reaction ensued and a liquid distilled over; this was poured back, and the whole cohobated for half an hour: a hydrocarbon then distilled over, together with a foetid liquid boiling up to about 300°. By fractional distillation a hydrocarbon was separated, which was but little affected by sulphuric acid; after treatment with this reagent and distillation over sodium, this boiled at 175°—178°, and possessed all the properties of cymene; the yield of pure hydrocarbon was about 25 per cent. of the absinthol employed.

0.2675 gram gave 0.8765 CO₂ and 0.261 H₂O.

	Calculated.		Found.
C ₁₀	120	89.55	89.35
H ₁₄	14	10.45	10.84
C ₁₀ H ₁₄	134	100.00	

Hence this product was formed by the removal of the elements of water just as the cymene formed by the action of zinc chloride.

The portions of the distillates boiling between 200° and 300° , were further fractionated; the portion boiling at 233° — 240° gave these numbers; it only constituted about 8 per cent. of the oil used.

0.248 gram gave 0.668 CO_2 and 0.199 H_2O .

	Calculated.		Found.
C_{10}	120	72.29	73.43
H_{14}	14	8.43	8.91
S	32	19.28	—
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$\text{C}_{10}\text{H}_{13}\cdot\text{SH}$	166	100.00	

Probably a small quantity of hydrocarbon was present in this distillate.

When dissolved in alcohol, and added in excess to silver nitrate solution, a *yellow* salt, very sparingly soluble in boiling alcohol, was thrown down: this gave the following numbers:

0.2260 gram gave 0.0880 Ag.

Ag = 38.94 per cent.

Calculated for $\text{C}_{10}\text{H}_{13}\cdot\text{SAg}$ 39.56 „

On the other hand, when the silver nitrate was in excess, a *white* salt was thrown down, of which

0.3640 gram gave 0.1780 Ag.

Ag = 48.89 per cent.

Calculated for $\text{C}_{10}\text{H}_{13}\cdot\text{SAg} + \text{AgNO}_3$ 48.76 „

When the alcoholic solution was boiled with mercuric oxide, the liquid (filtered hot) deposited on cooling shining needles containing mercury: in all respects, therefore, this product appears identical with the cymyl sulphhydrate described by Flesch, and obtained from camphor by the action of phosphorus sulphide.

B. Citronella distillates B and C mixed, were heated with phosphorus pentasulphide and distilled therefrom. On fractionating the resulting distillate, it was found to contain a hydrocarbon or mixture of hydrocarbons boiling between 160° and 180° , another boiling near 250° , and resinous substances of higher boiling-point. The lowest hydrocarbons after distillation over sodium, exhibited no constant boiling-point, and had a peculiar odour recalling burnt india-rubber; they amounted to about 30 per cent. of the oil used.

A. Fraction distilling at 159° — 165° , 0.1790 gram gave 0.573 CO_2 and 0.192 H_2O .

B. Fraction distilling at 173° — 180° , 0.1970 gram gave 0.637 CO_2 and 0.208 H_2O .

	Calculated.		Found.	
	A.	B.	A.	B.
C ₁₀	120	88·23	87·32	88·19
H ₁₆	16	11·77	11·91	11·73
<hr/> C ₁₀ H ₁₆	<hr/> 136	<hr/> 100·00		

The portions of distillate boiling between 220° and 240° did not give crystals of mercury-cymyl-sulphide on boiling in alcoholic solution with mercuric oxide, filtering hot, and cooling, nor did they precipitate with silver nitrate; whence it may be inferred that no appreciable quantity of cymyl sulphhydrate was found: a trace of a sulphur compound communicating a foetid smell was, however, present. On distillation over sodium, a portion distilling near 250° and other higher boiling liquids were obtained, apparently polymerides of terpenes (C₁₀H₁₆)_n. Cajeputol was found by Schmidl to form two terpenes boiling respectively at 160°—166° and 176°—178°, and polymerides thereof boiling above 300°.

Hence the action of phosphorus pentasulphide on the constituent C₁₀H₁₆O of citronella oil is to some extent analogous to that on absinthol; *i.e.*, the elements of water are removed in each case, producing a hydrocarbon—

The action of dehydrating agents on camphor and its two isomerides, myristicol and absinthol is thus alike; as shown in § 7, the cymene formed is the same in each case.*

§ 5. Action of Phosphorus Pentachloride on Citronellol.

When citronellol is cautiously dropped on to cooled phosphorus pentachloride phosphorus oxychloride is formed, with evolution of hydrogen chloride; a chlorinated organic substance is also produced, which breaks up when heated, evolving hydrochloric acid, and leaving a mixture of a terpene and a resinous polymeride thereof; the whole of the chlorinated body is not decomposed even by several distillations.

The lowest fractions of distillate, after washing with water, and long-continued heating with sodium, consisted of a terpene boiling between 168° and 173°, and yielding the following numbers:

0·2300 gram gave 0·740 CO₂ and 0·249 H₂O.

	Calculated.		Found.
	A.	B.	A.
C ₁₀	120	88·23	87·75
H ₁₆	16	11·77	12·02
<hr/> C ₁₀ H ₁₆	<hr/> 136	<hr/> 100·00	

* Notwithstanding that the principal constituents of the products of the action of phosphorus pentasulphide on citronellol are terpenes, further experiments have shown that some cymene is also formed, the quantity being greater the longer the action is continued.

Hence the reactions by which this body was formed are :

§ 6. Action of Bromine on Citronellol.

The oxidised constituent of citronella oil having the composition of a hydrate of a terpene, it appeared probable that it would unite with two proportions of bromine, and that the resulting dibromide would be capable of splitting up thus, forming water, hydrobromic acid, and cymene :—

These anticipations were realised, but a considerable quantity of non-volatile resin was also formed.

By the addition of the bromine to the citronellol much heat is evolved; the resulting compound on heating evolves much hydrobromic acid, partly as gas, partly as an aqueous distillate; a hydrocarbon also distils which, after two or three distillations, treatment with sulphuric acid, and heating with sodium, appears to be pure cymene: this boiled for the most part at 175° — 177° , and gave the following numbers on analysis :—

0.2885 gram gave 0.941 CO_2 and 0.283 H_2O .

0.2295 gram gave 0.221 H_2O (CO_2 lost).

	Calculated.		Found.	
C_{10}	120	89.55	88.94	—
H_{14}	14	10.45	10.89	10.69
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$\text{C}_{10}\text{H}_{14}$	134	100.00		

It is proposed to examine this reaction in the case of cajeput oil and other analogous bodies.

§ 7. Oxidation-products of Cymene from Absinthol and from Citronellol.

The cymene obtained as above by the action of phosphorus pentasulphide on absinthol, and that obtained as in the last section, were oxidised by chromic liquor; in each case nothing but terephthalic and acetic acids and carbon dioxide were formed, the yield of the former being about 35 per cent. in the first case, and 30 per cent. in the second.

The terephthalic acid obtained gave these numbers :

A. From absinthol, 0.4010 gram gave 0.846 CO_2 and 0.139 H_2O

B. „ citronellol, 0.3760 „ 0.800 „ 0.136 „

Calculated.			Found.	
			A.	B.
C ₈	96	57·83	57·54	58·02
H ₆	6	3·62	3·85	4·02
O ₄	64	38·55	—	—
<hr/> C ₈ H ₆ O ₄ ..	<hr/> 166	<hr/> 100·00		

The silver acetate obtained gave the following numbers :

A. From absinthol, 0·4305 gram gave 0·2780 Ag.

B. From citronellol, 0·5105 „ 0·3295 Ag.

Calculated for Ag acetate.

Ag = 64·68 per cent.

A.

64·58

B.

64·54

Taking together these circumstances and the boiling-point, and other properties of the cymenes thus formed, it is concluded that the cymene produced in these two instances is identical with the previously known form of cymene.

While this paper was in progress, Beilstein and Kupffer published a research on wormwood oil (*Deut. Chem. Ges. Ber.*, vi, 1183). Their results are in some respects identical with the above, as they find that oil of wormwood contains a small quantity of a terpene boiling below 160°, and that the main constituent, absinthol, when treated with phosphorus pentasulphide, forms cymene, which appears to be identical with that from cummin oil and that from camphor, as all three yield a sulpho-acid, forming the same salts of barium, lead, and calcium.

They give the boiling-point of absinthol as 195°; Gladstone states it as 217°; Leblanc, 204°; whilst the specimen examined above distilled entirely between 200° and 201° (corrected). They also give the boiling-point of cymene as 175°; the author has always found a slightly higher value, the mean result being 176·5°.