

XXII.—*Isomeric Terpenes and their Derivatives.* Part I.

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THE experiments detailed below were commenced some two years ago in the hope of obtaining some insight into the nature of the internal differences which exist between the various members of the terpene family.

In order to obtain two well-marked isomerides as subjects for the first series of experiments, the terpenes occurring in the essential oils of nutmeg and orange-peel were chosen, firstly because Gladstone found their boiling-points to be  $167^{\circ}$  and  $174^{\circ}$  respectively (*Chem. Soc. Journ.* [2] ii, 1, and x, 1), wherefore it appeared that both substances are different from oil of turpentine (boiling at  $160^{\circ}$ ), and secondly because the comparatively low price of these oils renders it more easy to obtain genuine specimens.

The oils used were obtained from Messrs. Piesse and Lubin, and were not only believed by Dr. S. Piesse to be pure and unadulterated, but were found, by careful proximate analysis and fractional distillation, to be at any rate free from fatty oils, and from turpentine.

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

About a kilogram of oil was slowly distilled; the greater part came over below  $200^{\circ}$ , but some distilled at  $290^{\circ}$ , a soft brown resin being left in the retort. This constituted 2 per cent. of the oil and gave on analysis carbon 77.9, hydrogen 9.4, agreeing with the formula  $C_{40}H_{56}O_5$ .

The highest portions of distillate obtained, viz., at  $260^{\circ}$ — $280^{\circ}$  and  $280^{\circ}$ — $290^{\circ}$ , gave respectively carbon 73.1, hydrogen 7.9, and carbon 72.9, hydrogen 8.1, agreeing with the formula  $(C_{10}H_{13}O_2)_n$ .

The lower portions of the first distillate were several times fractionally distilled, with the result of producing a considerable quantity of a mixture of hydrocarbons boiling below  $180^{\circ}$  and a small quantity

of an oxidised constituent boiling above  $210^{\circ}$ , apparently the "myristicol" of Gladstone. After several fractionations, however, it became evident that this substance alters by the action of heat, becoming changed first into fluids of the same composition, but higher boiling point, and finally into a semi-solid resin not volatile at  $300^{\circ}$ . The purest myristicol obtained boiled at  $212^{\circ}$ — $218^{\circ}$ ; this substance, and the higher polymerides obtained by repeatedly distilling it, gave on analysis numbers approximating more closely to the formula  $C_{10}H_{16}O$  than to any other probable formula.

(1.) Myristicol boiling at  $212^{\circ}$ — $218^{\circ}$ —

0.3005 gave 0.868  $CO_2$  and 0.280  $H_2O$ .

(2.) Another specimen—

0.2450 gram gave 0.7035  $CO_2$  and 0.228  $H_2O$ .

(3.) Portion of boiling point  $250^{\circ}$ — $265^{\circ}$ , obtained from (1) by repeated distillation—

0.2325 gram gave 0.674  $CO_2$  and 0.215  $H_2O$ .

(4.) Resin not volatile at  $300^{\circ}$  obtained from (1) by repeated distillation—

0.2530 gram gave 0.737  $CO_2$  and 0.229  $H_2O$ .

	Calculated.		(1.)	(2.)	(3.)	(4.)
$C_{10}$ . . . .	120	78.94	78.8	78.3	79.1	79.4
$H_{16}$ . . . .	16	10.53	10.3	10.3	10.3	10.1
$O$ . . . . .	16	10.53				
<hr/> $C_{10}H_{16}O$	<hr/> 152	<hr/> 100.00				

From these numbers it appears that "myristicol" contains as principal constituent a body isomeric with camphor, but differing from that substance in its physical properties, and notably in its power of becoming polymerized by heat. In a future paper it will be shown that both myristicol and camphor are alike in some respects, inasmuch as by the action of phosphorus pentachloride they give rise to chlorinated products,  $C_{10}H_{15}Cl$ , which split up by heat into hydrogen chloride and ordinary cymene.

The hydrocarbons boiling below  $180^{\circ}$ , separated from the nutmeg oil by fractional distillation as above mentioned, were heated for some time in contact with sodium, and then submitted to a careful fractional distillation over that metal for some weeks; finally the whole was almost entirely split up into two portions, one constituting about three-fourths of the whole, and boiling at  $163^{\circ}$ — $166^{\circ}$ , and the other (about one-sixth as much in bulk) boiling at  $173^{\circ}$ — $177^{\circ}$ . Intermediate fractions were at first obtained, but by successive distillations these split

up almost wholly into the higher and lower portions. A small quantity (less than 1 per cent. of the oil employed) boiled at temperatures above  $179^{\circ}$ ; but this appeared to contain a trace of an oxidized ingredient not destroyed by the action of the sodium. Thus the following numbers were obtained:—

(A) Fraction at $163^{\circ}$ — $164^{\circ}$ (the great majority)	0.3305 gram gave 1.2305 CO and 0.407 $\text{H}_2\text{O}$ .
(B) " $164^{\circ}$ — $166^{\circ}$ (a considerable quantity)	0.2295 " 0.7430 " 0.2495 "
(C) " $173^{\circ}$ — $175^{\circ}$ (a few c.c.'s only)	0.3460 " 1.1210 " 0.3645 "
(D) " $175^{\circ}$ — $177^{\circ}$ (second maximum)	0.2930 " 0.9460 " 0.3060 "
(E) " $177^{\circ}$ — $179^{\circ}$ (a few c.c.'s only)	0.2590 " 0.8370 " 0.2720 "
(F) " $179^{\circ}$ — $181^{\circ}$ (a few drops only)	0.2550 " 0.8095 " 0.2770 "
(G) " $181^{\circ}$ — $185^{\circ}$ (ditto)	0.2765 " 0.8800 " 0.2980 "

	(A.)	(B.)	(C.)	(D.)	(E.)	(F.)	(G.)
Carbon . . . . .	88.24	88.28	88.35	88.04	88.12	86.58	86.80
Hydrogen . . . .	11.89	12.08	11.71	11.61	11.67	12.07	11.98
	100.13	100.36	100.06	99.65	99.79	99.65	98.78

The formula  $\text{C}_{10}\text{H}_{16}$  requires carbon 88.23, hydrogen 11.77, and the formula  $\text{C}_{10}\text{H}_{14}$  requires carbon 89.55, hydrogen 10.45.

These numbers indicate that, contrary to Gladstone's experiments, the hydrocarbon of oil of nutmeg is not a single body boiling at  $167^{\circ}$  and of formula  $\text{C}_{10}\text{H}_{16}$ , but a mixture of a terpene boiling at  $163^{\circ}$ — $164^{\circ}$  (corrected temperature) and a hydrocarbon, apparently cymene, boiling towards  $177^{\circ}$ .

The lowest fractions are not necessarily free from cymene, as the presence of even 14 per cent. of this hydrocarbon would scarcely modify the percentages of carbon and hydrogen. Thus—

$6\text{C}_{10}\text{H}_{16} + \text{C}_{10}\text{H}_{14}$  (14 per cent. cymene) requires  $\text{C} = 88.42$ ;  $\text{H} = 11.58$ .

the higher fractions, however, contain a large amount of this hydrocarbon, as—

$2\text{C}_{10}\text{H}_{16} + \text{C}_{10}\text{H}_{14}$  (33 per cent. cymene) requires  $\text{C} = 88.67$ ;  $\text{H} = 11.33$ .

The cymene thus contained was isolated by a process suggested to the writer by Dr. Hugo Müller, viz., treating the mixture with sulphuric acid so as to polymerize the terpene present, and then diluting with water and distilling in a current of steam. Perfectly pure cymene was thus obtained. The experiments relating to this substance will be given in a future communication. About 8 per cent. of pure cymene was actually obtained from the fraction boiling at  $163^{\circ}$ — $164^{\circ}$ , 12 or 14 per cent. being present, whence it appears that the circumstance that a hydrocarbon boiling between  $160^{\circ}$  and  $170^{\circ}$  gives numbers agreeing fairly with the formula  $\text{C}_{10}\text{H}_{16}$  is no proof that it is a homo-

geneous substance, that it does not contain several percentages of another hydrocarbon of different formula, *e.g.*, cymene.

On subjecting oil of turpentine to the same treatment, cymene has also been isolated from this substance, whence it appears that there is no proof that terpenes yield terephthalic acid by oxidation, the small quantities of that substance obtained by oxidising oils of turpentine, lemon, &c., being probably derived from cymene pre-existing in the oils; and hence the arguments proving that terpenes are in any way connected with benzene are not so numerous as supposed.

## § 2. *Oil of Orange-peel. Proximate Constituents.*

On distilling about half a kilogram of the oil it was found to commence boiling at  $175^{\circ}$ ; 97.2 per cent. came over below  $180^{\circ}$ ; the remaining 2.8 per cent. constituted a soft resin containing carbon 75.6, hydrogen 9.7, agreeing with the formula  $C_{20}H_{30}O_3$ . A few drops passed over between  $180^{\circ}$  and  $280^{\circ}$ ; the portion collected at  $240^{\circ}$ — $250^{\circ}$  contained carbon 76.7, hydrogen 10.9, agreeing with the empirical formula  $C_{40}H_{64}O_6$ . The portion passing over at  $210^{\circ}$ — $230^{\circ}$  appeared to be identical with myristicol, as it gave numbers agreeing with the formula  $C_{10}H_{16}O$ . Like myristicol it became polymerised by repeated heating, becoming transformed into an isomeric resin. This contained carbon 79.7, hydrogen 10.6. Owing to the extremely small proportion in which this constituent exists, it was not found practicable to obtain it in an absolutely pure state, and hence it is probable that the only appreciable point in which it differed from myristicol, *viz.*, odour, was caused by the presence of a small amount of some other substance.

From the apparent presence of a minute quantity of myristicol in orange-peel oil it might be perhaps expected that cymene might be contained in the hydrocarbon present in that oil; this does not, however, appear to be the case, as no terephthalic is obtainable from that hydrocarbon by oxidation. After several distillations over sodium, the orange-peel hydrocarbon boiled quite constantly at  $178^{\circ}$  (corrected; Gladstone found  $174^{\circ}$ ) and gave the following numbers:—

0.4135 gram gave 1.3370  $CO_2$  and 0.4495  $H_2O$ .

	Calculated.		Found.
$C_{10}$ .....	120	88.23	88.17
$H_{16}$ .....	16	11.77	12.08
$C_{10}H_{16}$ ....	136	100.00	100.25

Evidently, from its boiling point, this hydrocarbon (termed *hesperidene* by Gladstone) is not identical with the lowest-boiling nutmeg

terpene; similar oxidation-products are, however, obtainable from these two hydrocarbons.

Cymene was carefully sought for in this hydrocarbon by the method formerly described, viz., agitation with several times its weight of strong sulphuric acid, dilution with water after 24 hours' standing, and distillation in a current of steam. 200 grams of hydrocarbon thus treated yielded, as first distillate, about 5 c.c. of a hydrocarbon that was much blackened by a second treatment with sulphuric acid; after dilution and distillation, about 2 c.c. of hydrocarbon were obtained; this was treated a third time with sulphuric acid which still blackened it much; after distillation less than 1 c.c. was obtained; this was carefully oxidised by chromic solution, but no trace of terephthalic acid was produced; it is hence pretty evident that no appreciable quantity of cymene could have been present in the hydrocarbon.

It is noteworthy that the heat developed by agitating hesperidene with sulphuric acid is sensibly less than that produced by similarly treating the same quantities of sulphuric acid and the nutmeg hydrocarbon (A), boiling at  $163^{\circ}$ — $164^{\circ}$ , notwithstanding that this latter contains a considerable quantity of cymene which is not acted on. It was not found practicable to make any accurate determination of the amounts of heat actually given out; without doubt the difference in boiling point and in other properties, physical and chemical, of the two hydrocarbons is closely connected with the different amounts of potential energy thus apparently contained in equal weights of the bodies in question. The same phenomenon is noticeable when bromine is dropped into the two hydrocarbons; the nutmeg product develops much more heat than that from orange oil, combination to dibromides of formula  $C_{10}H_{16}Br_2$  being the main reaction in each case.

### § 3. *Action of Potassium Dichromate and Sulphuric Acid on the Hydrocarbons.*

#### *A. Hesperidene.*

The hesperidene employed was carefully distilled a large number of times over sodium, and *wholly* volatilised in an atmosphere of hydrogen below  $179^{\circ}$ . Several ounces of this pure hydrocarbon were submitted, in quantities of about half an ounce at a time, to the action of a large volume of 10 per cent. solution of potassium dichromate, enough sulphuric acid being added to saturate the metals of that salt; about a litre of solution being used to every 10 c.c. of hydrocarbon, and the whole being boiled for several days in a flask with an inverted condenser attached; much  $CO_2$  was evolved, and the oil diminished greatly in volume and became somewhat viscid: on careful examination of the chrome liquors, no trace of toluic or of terephthalic acid was found to

be produced in any case. The unattacked oil had a powerful odour of *mint*, which became more like that of *anise* on standing for some months: it was separated by a funnel, washed, and distilled; the greater part came over below  $180^{\circ}$ , and smelt like orange oil with a minty odour; a portion, however, was left, and did not wholly distil at the limits of the mercurial thermometer. This portion of higher boiling point resembled the similar mixtures obtained from nutmeg oil and pure orange oil, inasmuch as it appeared to consist chiefly of a portion boiling near  $215^{\circ}$ , of formula  $C_{10}H_{16}O$ , acquiring a higher boiling point without appreciable change of composition on continued heating; it had a powerful smell of mint when fresh.

The total quantity of the portion of higher boiling point thus obtained was very small, not constituting more than 1 per cent. of the hydrocarbon employed; it was not, however, precontained in the hydrocarbon used, as this was *wholly* volatile below  $179^{\circ}$ .

The following numbers were obtained:—

A. Portion unattacked by chrome liquor fractionally distilled until all boiling below  $210^{\circ}$  was separated.

Portion boiling at  $210^{\circ}$ — $220^{\circ}$ .

0.170 gave 0.487  $CO_2$  and 0.1335  $H_2O$ .

B. Similar portion from another set of experiments.

0.301 gave 0.869  $CO_2$  and 0.272  $H_2O$ .

C. A and B mixed together, and distilled several times, acquired a higher boiling point, a few drops distilling at  $240^{\circ}$ — $250^{\circ}$ , and a little resin not volatile at  $300^{\circ}$  being left in the retort.

Distillate at  $240^{\circ}$ — $250^{\circ}$ . 0.1945 gave 0.561  $CO_2$  and 0.174  $H_2O$ .

		Found.			
		Calculated.	A.	B.	C.
$C_{10}$ , . . . . .	120	78.94	78.1	78.7	78.7
$H_{16}$ . . . . .	16	10.53	10.0	10.1	10.0
O . . . . .	16	10.53	—	—	—
$C_{10}H_{16}O$ ..	152	100.00			

The above results indicate that by the oxidizing action of chromic solution on hesperidene, a portion of the hydrocarbon becomes transformed into a body which, if not identical with myristicol and with the camphor contained in small proportion in orange-peel oil, differs from them only in the matter of odour, *i.e.*, that a hydrocarbon has been transformed by direct oxidation into a body which appears to possess the nature of an alcohol.

The majority of the hydrocarbon employed in the above experiments

appeared to be completely oxidized to carbonic acid and water. On distilling the chromic liquors, an acid distillate which reduced silver salts on boiling was obtained: the barium salt of the contained acid was made, and from it the silver salt by precipitation with silver nitrate. After recrystallisation from boiling water the silver salt gave numbers showing that the acid was pure acetic acid.

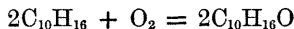
0.309 gram gave 0.2000 Ag.

Silver found. . . . . 64.7 per cent.

Calculated for acetate. . . 64.7 per cent.

Acetic acid, therefore, and probably a trace of formic was produced; the quantities of these acids found, however, bore a very small proportion to the hydrocarbon oxidized.

Berthelot has shown that when camphene is oxidized by platinum black, there is produced a small quantity either of camphor or of an isomeride thereof by the direct addition of oxygen—



(*Jahresbericht*, 1858, 441).

The resinizing of hydrocarbons from essential oils on keeping is probably due to the gradual absorption of oxygen and the polymerization of the  $C_{10}H_{16}O$  products thus formed.

In order to be perfectly certain that terephthalic acid is not a product of the *complete* oxidation of hesperidene, 50 grams of hydrocarbon were completely oxidized by boiling for several days with a mixture of 2 parts potassium dichromate and 3 of strong sulphuric acid with a bulk of water equal to three times that of the acid: *no trace of terephthalic acid was produced.*

#### *B. Lowest-boiling Hydrocarbon of Nutmeg Oil.*

The lowest fraction ( $163^{\circ}$ — $164^{\circ}$ ) of the previously-described nutmeg hydrocarbons was treated with chromic liquors precisely as the hesperidene just described. Carbonic and probably formic acid were produced, together with a small quantity of an acid which had all the characters of terephthalic acid (which, as will be shown in the next section, is producible from this fraction by the action of nitric acid). The apparently unattacked hydrocarbon was found on distillation to contain a small quantity of an oxidized substance closely resembling myristicol, the camphor contained in orange-peel oil, and the isomeride of myristicol (?) obtained by oxidizing hesperidene as above described: the few drops obtained boiled above  $210^{\circ}$ , and gave the following numbers:—

0.328 gram gave 0.9445  $CO_2$  and 0.308  $H_2O$ .



	Calculated.		Found.
C <sub>10</sub> .....	120	78·94	78·53
H <sub>16</sub> ....	16	10·53	10·43
O .....	16	10·53	—
<hr/>			
C <sub>10</sub> H <sub>16</sub> O	152	100 00	

The only difference perceptible between these four bodies, each expressed by the formula C<sub>10</sub>H<sub>16</sub>O, lay in their odours, each one being distinct from the others in this respect; it is hence believed that either all four are essentially identical, the difference in odour being due to very minute quantities of other products present along with the main constituent C<sub>10</sub>H<sub>16</sub>O; or else that the isomerism between them is very faintly marked, and that there must be some close internal connection between them.

The chromic liquors yielded, on distillation, an acid liquid; this was neutralised by fresh silver carbonate and the silver salt recrystallised from boiling water.

0·5265 gram gave 0·3390 Ag.

Silver found . . . . . 64·4 per cent.

Calculated for acetate . . . . 64·7 „

With the exception, therefore, of terephthalic acid (which, as previously pointed out, is probably wholly derived from the admixed cymene) the substances produced by oxidation with chromic solution of hesperidene and of the lowest boiling hydrocarbon of nutmeg oil, are either identical or closely akin, being acetic, formic, and carbonic acids, together with a body of formula C<sub>10</sub>H<sub>16</sub>O in each case.

#### § 4. Action of Nitric Acid on the Hydrocarbons.

##### A. Hesperidene.

Schwanert has shown (*Ann. Chem. Pharm.*, 128, 77) that when camphor and certain other analogous oxidized substances are treated with nitric acid, there is produced, *inter alia*, a non-crystalline acid, *camphresic acid* = C<sub>10</sub>H<sub>14</sub>O<sub>7</sub>. Kachler, however, finds (*Ann. Chem. Pharm.*, 159, 281) that the so-called camphresic acid from camphor consists essentially of a crystallisable acid of formula C<sub>9</sub>H<sub>14</sub>O<sub>6</sub> (C<sub>9</sub>H<sub>12</sub>O<sub>5</sub> when dried at 100° or distilled), to which he gives the name of *camphoronic acid*: this is characterised by giving a sandy tribasic barium salt precipitated only on boiling. As Schwanert states that his camphresic acid is also obtainable from certain hydrocarbons of the C<sub>10</sub>H<sub>16</sub> family (*e.g.*, from citrene), it might be expected that this acid would be obtainable from hesperidene, and from the nutmeg hydrocarbon; bodies of similar physical character are indeed obtainable, but their



compositions appear to agree neither with camphresic acid nor with camphoronic acid.

On slowly dropping hesperidene into 8 or 10 times its bulk of a boiling mixture of equal volumes of nitric acid and water, a vigorous action takes place, red fumes being copiously evolved, and the hydrocarbon becoming partially transformed into a brown resinous substance which on further treatment partially disappears and becomes yellow: an inverted condenser should be attached to the reaction flask to avoid loss of hydrocarbon.

When the action of the nitric acid has almost ceased, a pale yellow, hard, resinous substance is left, of which a small portion dissolves in ammonia. The undissolved portion gave on analysis carbon 59·3, hydrogen 6·1; nitrogen being also indicated as present by the sodium test.

The ammoniacal solution was dark-red brown in colour; after treatment with purified bone-black the partly decolorised liquid deposited amorphous flakes on supersaturation with nitric acid; these flakes somewhat resembled terephthalic acid, but had a very different composition. On boiling the ammoniacal solution with pure animal charcoal until it was almost wholly decolorised, the filtrate was found to give no precipitate with acids, showing that the whole of the dissolved substance had been taken up by the charcoal. Hence this dissolved portion could not have been terephthalic acid. The following numbers were obtained:—

- A. Crude yellow substance precipitated from ammoniacal solution,  
0·4065 gram gave 0·687 CO<sub>2</sub> and 0·164 H<sub>2</sub>O.  
B. Precipitated after most had been decolorised by animal charcoal,  
0·232 gram gave 0·406 CO<sub>2</sub> and 0·096 H<sub>2</sub>O.

	A.	B.
Carbon .....	46·1	47·7
Hydrogen .....	4·4	4·6

Nitrogen was found in specimen A by the sodium test.

Terephthalic acid contains—

Carbon .....	57·84
Hydrogen .....	3·61

Even supposing the yellow substance had been pure terephthalic acid, it would have amounted to only 0·2 to 0·3 per cent of the hydrocarbon used.

From the above results, together with the fact that no terephthalic acid is obtainable by means of chromic liquor, it is inferred that *hesperidene yields no terephthalic acid at all by oxidation.*

The nitric acid solution separated from the undissolved yellow resin was evaporated to dryness on the water-bath, the residue dissolved in

water, filtered, and neutralized by ammonia; barium nitrate added in the cold gave a copious precipitate of *oxalate*, from which the acid was obtained by treatment with sulphuric acid. The crystallised acid was analysed, and the acid recognised by the explosibility of its silver salt, and the examination of its calcium salt.

0·829 gram, dried at 100°, gave 0·569  $\text{CaCO}_3$ , and on ignition, 0·322  $\text{CaO}$ .

Calculated from  $\text{CaCO}_3$  .....  $\text{Ca} = 27\cdot4$  per cent.

„ „  $\text{CaO}$  .....  $\text{Ca} = 27\cdot7$  „

The formula  $\text{C}_2\text{O}_4\text{Ca}\cdot\text{H}_2\text{O}$  requires..  $\text{Ca} = 27\cdot4$  „

The filtrate from the barium oxalate when heated to boiling gave a trifling sandy precipitate, but this was found to be nothing but a little barium oxalate; no trace of Kachler's camphoronic acid could be found. Lead nitrate gave a copious yellow precipitate, from which, by means of sulphuretted hydrogen, a syrupy acid was obtained; this acid was soluble in ether, the ethereal solution leaving a thick syrup, which, on standing several months, became semi-solid. No crystals, however, could be obtained from the mass either by pressure in bibulous paper or by washing with small quantities of water, &c. This product, however, was not perfectly homogeneous; on boiling with marble powder it furnished a neutral solution, which yielded by evaporation an amorphous gummy calcium salt containing 17·0 and 17·2 per cent. calcium when dried at 100°, and 18·1 and 18·1 per cent. when dried at 160°.

This calcium salt was dissolved in water and precipitated by addition of alcohol, which threw down bulky amorphous flakes; the filtrate from these evaporated to dryness gave a very hygroscopic calcium salt fusible at 100°, and decomposing with emission of a peculiar odour at higher temperatures.

0·593 gram, dried at 100°, gave 0·140  $\text{CaSO}_4$ .  $\text{Ca} = 6\cdot94$  per cent. The precipitated calcium salt dried up to a gum-like mass and yielded the following numbers:—

0·4785 gram dried at 100° lost 0·0540 at 160° and gave 0·301,  $\text{CaSO}_4$ .

0·5865 gram dried at 160° gave 0·4120,  $\text{CaSO}_4$ .

The salt dried at 160° gave.....calcium = 20·85 per cent.

„ „ „ ..... = 20·67 „

„ at 100° „ ..... = 18·50 „

Moisture lost at 160° ..... = 11·28 „

The acid was obtained from this calcium salt by addition of sulphuric acid to its solution and extraction with ether; a syrup was thus obtained which became a mass of minute crystals on standing over sulphuric

acid for some months; on solution in water, however, no crystals could be obtained, but only a syrup becoming crystalline after several weeks only.

The following numbers were obtained:—

Acid dried over sulphuric acid for three months—

A. 0.3190 gave 0.483 CO<sub>2</sub> and 0.155 H<sub>2</sub>O.

B. 0.4555 gave 0.701 CO<sub>2</sub> and 0.2185 H<sub>2</sub>O.

Acid dried at 100°—

C. 0.4150 gave 0.670 CO<sub>2</sub> and 0.196 H<sub>2</sub>O.

D. 0.5190 gave 0.8535 CO<sub>2</sub> and 0.2385 H<sub>2</sub>O.

Calculated.			Found.		Calculated.			Found.	
			A.	B.				C.	D.
C <sub>20</sub> .....	240	41.81	41.29	41.97	C <sub>20</sub> .....	240	44.61	44.03	44.85
H <sub>30</sub> .....	30	5.23	5.39	5.33	H <sub>26</sub> .....	26	4.83	5.25	5.11
O <sub>19</sub> .....	304	52.96	—	—	O <sub>17</sub> .....	272	50.56	—	—
C <sub>20</sub> H <sub>26</sub> O <sub>17</sub> .2H <sub>2</sub> O	574	100.00	—	—	C <sub>20</sub> H <sub>26</sub> O <sub>17</sub>	538	100.00	—	—

The calcium salt, C<sub>20</sub>H<sub>20</sub>Ca<sub>3</sub>O<sub>17</sub>, requires 18.41 per cent. calcium.

Found 18.50       ,,       ,,

At 160° this salt loses 4H<sub>2</sub>O, becoming C<sub>20</sub>H<sub>12</sub>Ca<sub>3</sub>O<sub>13</sub>.

Calculated percentage of calcium ..... 20.69 per cent.

Observed ditto ..... { 20.85       ,,  
20.67       ,,

Calculated loss ..... = 11.04       ,,

Observed ..... = 11.28       ,,

It is hence evident that this acid is identical neither with camphresic acid nor with camphoronic acid, these acids requiring the following numbers:—

	Camphresic C <sub>10</sub> H <sub>14</sub> O <sub>7</sub> .	Camphoronic C <sub>9</sub> H <sub>14</sub> O <sub>6</sub> .	C <sub>9</sub> H <sub>12</sub> O <sub>5</sub> .
Carbon .....	48.78	49.54	54.00
Hydrogen .....	5.69	6.42	6.00
C <sub>10</sub> H <sub>11</sub> Ca <sub>3</sub> O <sub>7</sub> requires 19.80 p. c. Ca.		C <sub>9</sub> H <sub>9</sub> Ca <sub>3</sub> O <sub>5</sub> requires 23.34 per cent.	
		C <sub>9</sub> H <sub>10</sub> Ca <sub>2</sub> O <sub>5</sub> ,,       16.81       ,,	

To indicate its origin and its mode of formation (analogous to that of camphresic acid) it is proposed to term this acid *hesperisic acid*.

(B.) Lowest boiling fraction from nutmeg oil.

On treating this fraction in the above described manner results are

obtained precisely similar to those observed with hesperidene; a much larger quantity of resinous matter unattacked by nitric acid is, however, formed, and of this the majority is soluble in ammonia. After decolorisation by animal charcoal, a perfectly white precipitate is obtained on adding nitric acid to the ammoniacal solution; this consists of a mixture of toluic and terephthalic acids.

In a carefully conducted experiment 105·8 grams of hydrocarbon gave 14·0 of purified mixture, or 13·2 per 100 of hydrocarbon; as previously pointed out, these acids are probably produced from cymene still retained by the hydrocarbon in spite of long continued fractional distillation. This mixture gave on analysis 59·8 per cent. carbon, and 4·7 per cent. hydrogen, agreeing with the mixture,  $4\text{C}_8\text{H}_8\text{O}_4 + \text{C}_8\text{H}_8\text{O}_2$ , which requires carbon 60·0 per cent., hydrogen 4·0 per cent.

In another experiment where the fractional distillation had not been carried so far, and where consequently a larger proportion of cymene was contained, 15·7 parts of mixed acids per 100 of hydrocarbon were obtained, the mixture containing  $4\text{C}_8\text{H}_8\text{O}_2 + 3\text{C}_8\text{H}_8\text{O}_4$ .

Found, Carbon = 64·3 and 64·2 per cent. : calculated 64·5  
 „ Hydrogen = 5·1 and 4·9 „ : „ 4·8

It was found extremely difficult to effect a satisfactory separation of the two acids: in boiling water or alcohol toluic acid readily dissolves, whilst terephthalic acid is almost insoluble in these menstrua; in the case of a mixture of the two acids, however, a considerable amount of terephthalic acid is taken up by the toluic acid solution, whilst on the other hand a certain quantity of toluic acid is always left behind in the undissolved terephthalic acid, even after many treatments with boiling water or alcohol.

Even the purest toluic acid obtained after ten crystallisations from boiling water, retained about 20 per cent. of terephthalic, containing carbon, 67·6; hydrogen, 5·8 ( $4\text{C}_8\text{H}_8\text{O}_2 + \text{C}_8\text{H}_8\text{O}_4$  requires carbon, 67·6; hydrogen, 5·4).

To obtain the terephthalic acid pure, the portion insoluble in boiling water was boiled for 24 hours with a mixture of 3 parts sulphuric acid, 5 of water, and 2 of potassium dichromate; the unoxidized portion was dissolved in ammonia and precipitated by hydrochloric acid several times; a snow-white mass was finally obtained which after drying at 100° gave the following numbers:—

0·3205 gram gave 0·679  $\text{CO}_2$  and 0·110  $\text{CO}_2$ .

	Calculated.		Found.
$\text{C}_8$ .....	96	57·83	57·78
$\text{H}_8$ ....	6	3·62	3·88
$\text{O}_4$ .....	64	38·55	—
$\text{C}_8\text{H}_8\text{O}_4$ ..	166	100·00	

The barium salt was also made—

0.515 gram gave 0.3935 BaSO<sub>4</sub>.

Ba.....	= 44.9
Calculated .....	= 45.5

This acid exhibited no tendency to melting when heated, but sublimed unaltered; it was carefully examined to see if any small trace of an acid isomeric with terephthalic acid was present; the barium salt, however, yielded nothing but unaltered terephthalic acid when digested with cold water, filtered, and precipitated by hydrochloric acid; similarly nothing but terephthalic acid was dissolved by boiling water. It hence appears that the toluic acid produced simultaneously with the terephthalic acid is only ordinary toluic acid yielding terephthalic acid by further oxidation, which might be expected, as both acids are probably derived from cymene in the hydrocarbon used.

The nitric acid filtrate from the crude toluic and terephthalic acids was treated precisely as the corresponding filtrate from the oxidation of hesperidene. A quantity of barium oxalate was thus obtained from which the calcium salt was prepared as before.

0.372 gram gave 0.259 CaCO<sub>3</sub> (after being dried at 100°).

Found.....	Ca = 27.8 per cent.
Calculated for CaC <sub>2</sub> O <sub>4</sub> ,H <sub>2</sub> O.	27.4 per cent.

No trace of Kachler's camphoronic acid could be obtained from the filtrate from the barium oxalate; after conversion into lead salt, decomposition by sulphuretted hydrogen, and extraction with ether, a sour syrup was obtained very similar to that obtained from hesperidene; this was converted into calcium salt, and the solution precipitated by alcohol; the precipitated calcium salt resembled the one similarly obtained from hesperidene, but yielded the following numbers:—

(A) 0.5380 gram dried at 100°, lost 0.031 at 160°, and gave 0.342 CaSO<sub>4</sub>.

(B) 0.5260 gram dried at 100°, lost 0.0315 at 160°, and gave 0.334 CaSO<sub>4</sub>.

	(A.)	(B.)
Percentage of calcium in salt dried at 100° ....	18.70	18.67
"                    "                    160° ....	19.84	19.86
"            water lost at 160° .....	5.76	5.99

From this precipitated calcium salt the acid was obtained by treatment with sulphuric acid and ether; after drying over sulphuric acid for several weeks, it constituted a viscid syrupy honey-like mass, which gradually became a mass of small crystals closely resembling the acid obtained from hesperidene in appearance.

It yielded the following numbers :—

0.4220 gram lost 0.0280 at 100	Loss = 6.60 per cent.
0.3050 „ „ 0.0210 „	„ = 6.88 „
0.3940 gave (after drying at 100°)	0.669 CO <sub>2</sub> and 0.1835 H <sub>2</sub> O
0.2840 „ „ „ „	0.478 CO <sub>2</sub> and 0.138 H <sub>2</sub> O

	Calculated.		Found.	
C <sub>20</sub> .....	240	45.98	46.31	45.90
H <sub>26</sub> ....	26	4.98	5.17	5.39
O <sub>16</sub> .....	256	49.04	—	—
<hr/> C <sub>20</sub> H <sub>26</sub> O <sub>16</sub>	<hr/> 522	<hr/> 100.00		

The substance dried over sulphuric acid was, therefore, C<sub>20</sub>H<sub>26</sub>O<sub>16</sub>.2H<sub>2</sub>O, the 2H<sub>2</sub>O being lost at 100°.

Calculated loss .....	6.45
Observed .....	{ 6.60
	{ 6.88

The calcium salt C<sub>20</sub>H<sub>20</sub>Ca<sub>3</sub>O<sub>16</sub>, requires 18.86 per cent. calcium.

Found (dried at 100°)	{ 18.70	„	„
	{ 18.67	„	„

When dried at 160°, this calcium salt appears to lose 2H<sub>2</sub>O, forming C<sub>20</sub>H<sub>16</sub>Ca<sub>3</sub>O<sub>14</sub>.

	Loss of H <sub>2</sub> O.	Per cent. of Ca.
Calculated .....	5.66	20.00
Observed .....	{ 5.76	19.84
	{ 5.99	19.86

It hence appears that the acid formed by oxidizing the lowest nutmeg hydrocarbon with nitric acid (which may be termed *myristic acid*), although similar to hesperic acid in composition and properties, is yet not identical with that acid, containing less oxygen; thus the two acids may be contrasted :—

	Myristic acid.	Hesperic acid.
Acid dried over sulphuric acid	C <sub>20</sub> H <sub>26</sub> O <sub>16</sub> .2H <sub>2</sub> O	C <sub>20</sub> H <sub>26</sub> O <sub>17</sub> .2H <sub>2</sub> O
„ at 100° .....	C <sub>20</sub> H <sub>26</sub> O <sub>16</sub>	C <sub>20</sub> H <sub>26</sub> O <sub>17</sub>
Calcium salt dried at 100° ..	C <sub>20</sub> H <sub>20</sub> Ca <sub>3</sub> O <sub>16</sub>	C <sub>20</sub> H <sub>20</sub> Ca <sub>3</sub> O <sub>17</sub>
„ „ at 160° ..	C <sub>20</sub> H <sub>16</sub> Ca <sub>3</sub> O <sub>14</sub>	C <sub>20</sub> H <sub>12</sub> Ca <sub>3</sub> O <sub>13</sub>

### § 5. Action of Hydriodic Acid on Hesperidene.

It was hoped that by combining hydriodic acid with terpenes, derivatives might be obtained from the products whose characters might

serve to elucidate the isomerism of the original hydrocarbons; the results obtained below with hesperidene, however, do not promise much advantage in this direction.

Hesperidene was brought in contact with gaseous hydriodic acid, which was absorbed in large quantity; the liquid freed from excess of acid by agitation with dilute caustic soda, gave on analysis numbers indicating a compound  $C_{10}H_{16}.HI$  mixed with a slight excess of  $C_{10}H_{16}$ ; no crystalline compound could be obtained by cooling or leaving it to stand.

This hydriodide decomposed by exposure to light or on heating, iodine being set free; it appeared to boil at about  $220^\circ$  with decomposition, hydriodic acid being evolved in small quantity; a portion, however, distilled unchanged mixed with regenerated and partially polymerised  $C_{10}H_{16}$ .

In the hope of adding on hydrogen to the terpene, the hydriodide was treated with phosphorus and water or hydriodic acid, but without success, a negative result only being obtained whether red or yellow phosphorus was employed, and whether the operation was conducted in a flask with an inverted condenser attached, or in a sealed tube heated to  $100^\circ$ ,  $130^\circ$ , or  $150^\circ$ ; phosphonium iodide and phosphoretted hydrogen were, however, produced in some little quantity, frequently giving rise to explosions. By heating the mixture for several hours in a flask with inverted condenser attached, the whole of the associated iodine was removed, and finally a mixture of phosphorus acids and a colourless oily hydrocarbon boiling at about  $150^\circ$ , was left; this was sparingly soluble in cold alcohol, rather more soluble in boiling alcohol; a sample precipitated from hot alcoholic solution by addition of water gave these numbers—

0.2620 gram gave 0.851  $CO_2$  and 0.267  $H_2O$ .

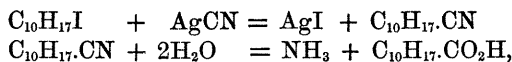
	Calculated.		Found.
$C_{15}$ . . . .	180	88.3	88.5
$H_{24}$ . . . .	24	11.7	11.3
<hr/>			
$C_{15}H_{24}$ . .	204	100.0	99.8

Hence it appears that the hesperidene had become partly polymerised by the action of the hydriodic acid, or perhaps by that of the phosphorus acids produced; Gladstone finds (*Chem. Soc. Journ.* [2], x, 1), that *cedrenes* (as bodies of  $C_{15}H_{24}$  formula may be conveniently termed), boil at  $249^\circ$  to  $260^\circ$ .

Hesperidene hydriodide prepared as above was dissolved in alcohol and boiled *per ascensum* with the equivalent quantity of silver cyanide for two hours, when almost all the silver compound had become transformed into iodide; the alcoholic solution had a peculiar odour,



recalling that of the nitriles. In the hope of obtaining a new acid by the reactions—



the alcoholic solution was boiled *per ascensum* with caustic potash for several hours; a copious disengagement of fishy-smelling ammonia ensued, and a minute quantity of the potash salt of a new acid was formed; the greater part of the hydriodide, however, became converted into a dirty brown tarry mass, which could not be purified; probably this was a polymeride =  $(\text{C}_{10}\text{H}_{16})_n$  formed by the splitting up of the nascent acid,  $\text{C}_{10}\text{H}_{17}\text{CO}_2\text{H}$ .

The potash-salt was dissolved in water and extracted with ether after souring with hydrochloric acid; a small quantity of a non-crystalline, non-volatile acid was obtained, apparently mixed with formic acid, as the liquid reduced silver salts on boiling, but lost that property after evaporation to dryness. Lead acetate gave a flocculent white precipitate which, after thorough washing, contained 54·6 per cent. of lead.

The neutral salt  $(\text{C}_{10}\text{H}_{17}\text{CO}_2)_2\text{Pb}$  would require lead = 36·3

And the basic salt  $(\text{C}_{10}\text{H}_{17}\text{CO}_2)_2\text{Pb}, \text{PbO}$  „ 53·7

This reaction appeared, consequently, so unpromising, that no further experiments have yet been made in connection with it; possibly the hydrochlorides and hydrobromides of the terpenes might give better results.

### § 6. Conclusion.

From the foregoing results, it is evident that turpentine oil (b.p. 160), the terpene of nutmeg oil (b.p. 163°), and hesperidene (b.p. 178), are three different isomerides, since the former gives camphresic acid by its oxidation (Schwanert); the number of formulæ conceivable for bodies  $\text{C}_{10}\text{H}_{16}$  is great, but it appears not impossible that many bodies now believed to be different and peculiar terpenes may, like “myristicene,” turn out, on closer inspection, to be mixtures, perhaps of previously known bodies. Further experiments on the nature of the isomerism in this series of compounds are in progress.

In conclusion, it gives me great pleasure to return thanks to Messrs. C. H. Piesse and G. H. Beckett, for much valuable assistance rendered during the earlier and later portions of these experiments respectively.