XXV.—*Note on Otto of Limes.*

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THIS oil is obtained from the rind of the fruit of the *Citrus limetta*, in the same way as the kindred ottos of orange and lemon, viz., by rasping the unripe fruits by rubbing them over a perforated concave metal rasp fixed over a basin. The pulp thus obtained is squeezed in a press and the otto which exudes purified by filtration; in this state it has the peculiar sweet sharp odour characteristic of the fruit. Ottos thus obtained are commercially more valuable than essential oils prepared by distillation from the same fruits, or from the residues left in this operation, having a more delicate perfume.

The specific gravity of the oil examined was found to be 0.90516 at 15.5°; when subjected to distillation a slight sputtering occurred due to the presence of a minute quantity of water; distillation commenced at 181°, and between this temperature and 186° about 70 per cent. of the oil passed over; only a minute quantity distilled between 186° and 250°, the residue, constituting a dark-brown gluey mass, giving indications of decomposition at higher temperatures; when cold it was a thick viscid soft resin, almost solid in consistency; after standing in the retort for three or four months a crystalline body began to appear in the midst of the resin and increased in amount for some two or three weeks; by the aid of the pump-filter these crystals were separated, with some difficulty, from the thick colophene-like matter; they were washed with some of the lowest distillate (181—186°), in which they dissolved but sparingly, and finally with a little alcohol of 90 per cent., in which they dissolved to some extent when cold, readily on boiling. The approximately pure crystals were straw-yellow and almost scentless; after crystallisation from boiling 90 per cent. alcohol and then twice from about 45 per cent. alcohol (equal volumes of strong alcohol and water), they were nearly white micaceous plates, quite destitute of odour, and melting at 162° (corrected). On combustion the following numbers were obtained agreeing best with the formula $C_{24}H_{25}O_5$:—

	0.2050 gram gave 0.5480 CO ₂ and 0.1360 H ₂ O			
	0.2290 ,, 0.6105 CO ₂ ,, 0.1480 H ₂ O			
	Calculated.		Found.	
C ₂₄	288	72.73	72.91	72.71
H ₂₅	28	7.07	7.37	7.18
O ₅	80	20.20	—	—
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	396	100.00		

Hence the body was not the hesperidin of Ed. Hoffmann (*Deut. Chem. Ges. Ber.*, 1876, 685), $C_{22}H_{26}O_{12}$, melting at near 245° ; on fusion with potash at about 230° it yielded no protocathechuic acid. Its alcoholic solution was perfectly neutral; in water it was insoluble, but in caustic potash solution it dissolved to a lemon-yellow fluid from which acids precipitated white micaceous crystals. On gently heating over the melting point it charred and gave off inflammable vapours, but could neither be distilled nor sublimed with decomposition.

The distillate below 186° was faintly yellow; on redistillation about 99 per cent. passed over almost constantly at 176° , a little of a colourless fluid exhibiting no constant boiling point, distilling between 180° and 230° , and only a minute quantity of resinous matter being then left in the distilling vessel. The boiling point of the main fraction was not sensibly altered by cohobation with sodium; hydrogen was, however, evolved during the process and a reddish flocculent substance separated which was not further examined. The distillate obtained after this treatment gave numbers showing that it was a hydrocarbon of the terpene family—

0.173 gram gave 0.558 CO_2 and 0.187 H_2O

	Calculated.		Found.
C_{10}	120	88.23	87.96
H_{16}	16	11.77	12.01
$C_{10}H_{16}$	136	100.00	

Hence otto of limes consists of a soft resin, not volatile at 250° , dissolved in somewhat more than twice its weight of a terpene boiling at 176° (uncorrected).

The terpene of orange oil (boiling at 178°) has been shown by one of us (this *Journal*, 1873, 686) to yield cymene readily by treatment with bromine in proportion to realize the equation—

the bromine being cautiously added to the terpene and the resulting dibromide, $C_{10}H_{16}Br_2$, being then heated in a flask with an inverted condenser attached. On the other hand, Oppenheim found (*Deut. Chem. Ges. Ber.*, v, 628) that citrene, the terpene of lemon oil boiling at 173 — 174° , and turpentine terpene boiling at 160 — 161° , do not yield cymene in any quantity by this mode of treatment, although they form about 30 per cent. of the calculated amount on heating with aniline in sealed tubes. An analogous result was also obtained by one of us (*loc. cit.*) with the terpene of nutmeg oil, myristicene, boiling at 163 — 164° . In order to see whether the

ease with which the dibromides $C_{10}H_{16}Br_2$ split up on heating into hydrobromic acid and cymene is connected with the boiling points of the terpenes, the lime terpene was converted into dibromide by cautious addition of the calculated amount of bromine. On heating the product torrents of hydrobromic acid escaped; the majority of the substance, however, was converted into a black pitch-like mass, but little cymene being formed. After heating until the evolution of hydrobromic acid nearly ceased, the substance was distilled and the small amount of distillate obtained purified by cohobation with sodium and finally by treatment with concentrated sulphuric acid and dilution with water; the oily layer which thus separated was again distilled over sodium; a hydrocarbon passed almost absolutely constantly at 176° and appeared to be cymene, but contaminated with a minute amount of some brominated compound (probably $C_{10}H_{15}Br$) which had resisted all the attempts at purification—

I. 0.2335 gram gave 0.746 CO_2 and 0.2275 H_2O

II. 0.309 ,, 0.989 CO_2 ,, 0.304 H_2O

	Calculated.		Found.	
C_{10}	120	89.55	87.13	87.28
H_{14}	14	10.45	10.82	10.93
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$C_{10}H_{14}$	134	100.00		

The yield of this hydrocarbon was not more than 10—15 per cent. of the terpene employed, whence it would seem that, notwithstanding the nearness of the boiling point of the lime terpene to that of hesperidene the two terpenes are very dissimilar, since hesperidene readily yields upwards of 80 per cent. of pure cymene by this mode of treatment. From the boiling point of the lime terpene and its behaviour in this respect it seems highly probable that it is identical with citrene, the terpene of the lemon.

The identity of the cymene prepared as above with ordinary cymene was established by oxidizing it with a mixture of sulphuric acid, water, and potassium dichromate; terephthalic and acetic acids were thus produced.