

XI. *On the Constitution of the Essential Oil of Rue.*

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THE essential oil procured by distillation of the rue plant with water, has already been examined by several chemists. It was analysed many years ago by WILL*, who deduced from his analyses the expression $C^{28}H^{28}O^3$. But at that time far too little was known about the oxygenated essential oils to permit of their accurate investigation. A more minute series of experiments, made by GERHARDT in 1848†, led him to conclude that oil of rue consisted principally of the capric aldehyde, contaminated by a small quantity of some hydrocarbon. This view was considered to be confirmed by the production of capric acid when the oil underwent oxidation by means of nitric acid. But the production of an acid containing C^{20} merely rendered it probable that the rue oil did not contain *less* than 20 equivalents of carbon; it was no proof that it did not contain *more*. In fact, the action of nitric acid varies with its concentration.

Guided by ideas which need not now be detailed, I made in 1853 some experiments, with the intention of obtaining from oil of rue certain bodies of the capric series, but they only served to convince me that the views then entertained regarding the constitution of the oil were erroneous. Some curious reactions were observed, but the experiments diverging into other channels have not, as yet, been renewed. Previous to recommencing them, it has been thought necessary to make a fresh examination of the oil; the results form the subject of this communication.

On examination of GERHARDT'S numbers, it will be found that, while two of his analyses agree exactly with the formula $C^{20}H^{20}O^2$, the vapour-density (5·83) exceeds the theoretical number (5·398) to a degree much greater than can be accounted for by an error of experiment; the number obtained being almost the correct value for the homologue C^2H^2 above the capric aldehyde. Moreover, the fluid analysed was purified by distillation only.

In this investigation use has been made of the invaluable reagent for the isolation and purification of aldehydes (and bodies of more or less analogous constitution), placed in the hands of chemists principally by the researches of M. BERTAGNINI. By its aid a perfect separation has been made of the aldehydes in oil of rue, enabling their nature to be clearly determined.

On submitting the crude oil to about a dozen fractional distillations, distillates were obtained from 160° to 238°. On treating them with the bisulphites of soda or ammonia,

* Ann. der Chem. und Pharm. xxxv. 235.

† Ann. de Chim. et de Phys. [3] xxiv. 103.

great differences became apparent in their behaviour. The portions boiling between 160° and 188° were scarcely affected; they floated above the solution of the bisulphite, and after contact for weeks, showed scarcely a trace of crystalline compound. The fluids boiling at intermediate points yielded more crystals as their point of ebullition became higher; and when a boiling-point of 210° was reached, the oil (treated as before) became semi-solid in about two hours; and from that temperature to 238° , the tendency to yield crystals on agitation with the bisulphites increased.

Bisulphite of ammonia was found to be a more convenient reagent than the corresponding salt of soda, the resulting salt being more crystalline, and procurable with greater ease in a state of purity. When the fractions distilling in the twelfth rectification at 232° and upwards were treated with bisulphite of ammonia, the whole solidified, in the course of twelve hours, to a crystalline mass of such firm texture, as to be with difficulty penetrated by a glass rod. The very last fractions distilling at 260° and upwards yielded less crystalline masses, retaining traces of an empyreumatic oil.

The analyses and vapour-density determinations described in this paper were all made upon fluids obtained by the following process. The crystalline substance from the lower fractions was thrown upon a filter, and well washed with a saturated solution of bisulphite of ammonia, which mechanically carried away much of the oily impurities. The product of this operation was a snow-white mass with a rich pearly lustre. It was carefully removed to a fresh piece of filtering-paper, and, a few folds intervening, laid upon a porous tile. In the course of a few hours the mass became firm enough to be removed, and being folded in several fresh pieces of filtering-paper, was again placed between tiles and subjected to considerable pressure. This was repeated until the paper ceased to receive any stain. The crystalline solid was then transferred to a stoppered vessel, and gently heated with a strong solution of potash. In a short time the compound was decomposed, the aldehyde floating on the surface in the form of an oil.

The aldehyde thus procured was colourless; it possessed a pleasing fragrance, totally different from the nauseous odour of the plant itself. Its boiling-point, as first prepared, fluctuated considerably, arising partly from oxidation and consequent formation of other bodies, and partly from the presence of a small portion of another aldehyde. The oxidation could only be prevented by performing the operation in a current of hydrogen, an exceedingly inconvenient process in fractional distillations, the apparatus having to be taken apart every few minutes. In the course of the experiments a considerable number of specimens were obtained, but they all had the same composition and vapour-density. By carefully collecting the residues of the distillations, and redistilling in minute retorts, blown from glass tubing, about sixty grains of the second aldehyde were obtained, still however contaminated by some of the fluid having the lower formula.

The first aldehyde yielded on analysis the following numbers:—

- I. .1982 gramme gave .5643 gramme carbonic acid and .2329 water.
- II. .2057 gramme gave .5843 gramme carbonic acid and .2475 water.

- III. ·2047 gramme gave ·5820 gramme carbonic acid and ·2349 water.
- IV. ·2212 gramme gave ·6320 gramme carbonic acid and ·2562 water.
- V. ·1986 gramme gave ·5662 gramme carbonic acid and ·2352 water.
- VI. ·2138 gramme gave ·6103 gramme carbonic acid and ·2501 water.
- VII. ·2131 gramme gave ·6077 gramme carbonic acid and ·2494 water.
- VIII. ·2128 gramme gave ·6067 gramme carbonic acid and ·2552 water.

	I.	II.	III.	IV.	V.	VI.	VII.	VIII.
Carbon	77·65	77·47	77·54	77·92	77·75	77·85	77·77	77·76
Hydrogen	13·05	13·37	12·75	12·87	13·16	13·00	13·00	13·32
Oxygen	9·30	9·16	9·71	9·21	9·09	9·15	9·23	8·92
	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>

	Mean.	Calculation.	
Carbon	77·71	C ²²	132 77·65
Hydrogen	13·07	H ²²	22 12·94
Oxygen	9·22	O ²	16 9·41
	<u>100·00</u>		<u>170</u> <u>100·00</u>

The above combustions were made in the manner described in the first part of my paper "On some of the Products of the Destructive Distillation of Boghead Coal*."

The annexed values were obtained in two determinations of the density of the vapour. In order to prevent oxidation, the balloon was in each case filled with hydrogen previous to immersion in the bath.

	I.	II.
Temperature of the air	18°	16°
Temperature of the vapour.	247°	259°
Pressure	760	759·2 mm.
Excess of weight of balloon	·2220	·5770 gramme.
Capacity of balloon	82·5	228·0 cub. cent.
Residual hydrogen	1·0	10·0 cub. cent.
Density of vapour	5·83	5·91

The formula C²² H²² O² = 4 volumes, requires—

22 volumes carbon vapour	0·8290 . 22 =	18·2380
44 volumes hydrogen	0·0692 . 44 =	3·0448
2 volumes oxygen	1·1056 . 2 =	2·2112
		<u>23·4940</u>
		4 = 5·8735

Experiment (mean).	Theory.
5·87	5·874

* Philosophical Transactions, 1857.

The first of these experiments yielded the same number as that found by GERHARDT. It is somewhat remarkable that the vapour-density did not induce him to adopt a formula with 22 instead of 20 equivalents of carbon.

The specific gravity of the fluid was 0·8497 at 15°. During a cold night the aldehyde was converted into a solid crystalline mass, resembling camphor. Agitation will cause it to solidify when the temperature is as high as 7°.

GERHARDT made four analyses and one vapour-density determination of oil of rue, and it is worthy of notice that two of his analyses and the vapour-density agree better with the view now proposed of its constitution than with his own. His analyses were as follows:—

	<i>a.</i>	<i>b.</i>	<i>c.</i>	<i>d.</i>
Carbon	77·65	77·69	76·95	77·10
Hydrogen	12·80	12·87	12·85	12·95
Oxygen	9·55	10·44	10·20	9·95
	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>	<u>100·00</u>

The analysis *a* was made on the first portion of the distillate, *b* and *c* on the last third, and *d* by treating an alcoholic solution of oil of rue with gaseous hydrochloric acid, and reobtaining the aldehyde by the addition of water. It would appear that this last operation (supposed by him to yield an isomeric modification of the capric aldehyde) was in fact to some extent a process of purification, the liquid so prepared having a fruity odour, different from the oil merely purified by distillation, and therefore resembling the pure and fragrant aldehyde obtained by me.

Although the experiments detailed scarcely permit a doubt of the true nature of the substance (especially when the mode of purification is considered), still it was wished to place the matter beyond dispute. With this intention, the aldehyde obtained from the crystalline bisulphite was again treated with bisulphite of ammonia, and the whole process of purification repeated. The annexed analysis was made upon the aldehyde so obtained.

·2112 gramme gave ·6015 carbonic acid and ·2458 water.

	Experiment.	Calculation.
Carbon	77·67	77·65
Hydrogen	12·93	12·94
Oxygen	9·40	9·41
	<u>100·00</u>	<u>100·00</u>

The existence of margaritic acid having been disproved, and it having been rendered certain that cocinic acid does not contain 22 equivalents of carbon, it follows that this is the first substance yet isolated belonging to the eleventh series of bodies homologous with the derivatives of the fatty acids. It is the hydruret of the negative radical euodyle* homologous with acetylene. When carefully purified by distillation, it distils at 213° C.

* From *εὐώδης*.

The quantity in my possession was too small to permit of an examination of its derivatives. I had hoped to obtain euodic acid by the action of weak nitric acid upon the aldehyde, but the oxidation proceeds too far, the carbon being attacked with formation of capric acid. A barium salt gave on analysis 29.985 per cent. of barium; caprate of barium requires 28.642. During the action of the nitric acid, especially if it be not very weak, pelargonic acid is formed. A small quantity was also obtained of another substance, which was separated in the following manner. The acid solution, and the oily layer produced by cohobating euodic aldehyde and ordinary nitric acid diluted with its own bulk of water, were separated by means of a tap funnel. The oily liquid, on treatment with a strong solution of potash, partly dissolved, but, on filtration, a soft yellow substance remained on the paper. It dissolved in boiling alcohol, and separated on cooling in brilliant yellow spangles, exactly resembling chrysène as it appears when crystallized from Boghead naphtha. On examination it appeared to be the potassium salt of the highly singular substance described by CHIOZZA*, and which he regards as a compound of pelargonic acid with binoxide of nitrogen. He states that great difficulties were found in its analysis, owing to the strong tendency of the nitrogen, in the state in which it exists in the acid, to form nitrous or nitric acid, which, entering the potash apparatus, increases its weight, and in consequence causes the carbon to come out too high. The entire quantity at my disposal being only 0.2170 gm., a correct result on combustion was scarcely hoped for, especially as 0.02 had been used in a few almost microscopic preliminary experiments. The following result is, nevertheless, sufficient to identify the substance with that described by CHIOZZA.

·1976 gramme gave ·3135 carbonic acid and ·1282 water.

		Calc. C ¹⁸ H ¹⁷ KN ² O ⁸ .
Carbon	43.3	42.20
Hydrogen . . .	7.2	6.64

By carefully treating the residues of the distillates, previously alluded to, a small quantity of the lauric aldehyde was obtained. It was not quite free from euodic aldehyde. Its boiling-point is about 232° C. The following is the result of its analysis:—

·1986 gramme gave ·5686 carbonic acid and ·2310 water.

Experiment.		Calculation.	
Carbon	78.1	C ²⁴ 144	78.26
Hydrogen . . .	12.9	H ²⁴ 24	13.04
Oxygen	9.0	O ² 16	8.70
	<u>100.0</u>	<u>184</u>	<u>100.00</u>

The density of its vapour was found to be 6.182, a number considerably below that required by theory (6.366), but quite high enough, taken in conjunction with the analysis, to show the presence of lauric aldehyde in oil of rue.

* Compt. Rend. xxxv. 797 (1852).

The fluids accompanying the aldehydes in oil of rue were found not to be of much interest. That portion boiling at 154° was the most volatile. It evidently belongs to the already too numerous groups of bodies isomeric with oil of turpentine. It was not obtained quite free from an oxygenated oil. By repeated rectifications a portion was obtained yielding,—

	I.	II.
Carbon	84.63	84.88
Hydrogen	11.91	11.90
Oxygen	3.46	3.22
	100.00	100.00

By cohobation over a fluid alloy of potassium and sodium, a portion of oxygen was removed without decomposition of the oil. Thus purified, a combustion gave—

Carbon	86.20
Hydrogen	12.16
Oxygen	1.64
	100.00

But it was impossible to remove the whole of the oxygen in this manner; and although the object could have been attained by other methods, the trouble would have been out of proportion to the result.

Oil of rue contains, in addition to the aldehydes and terebinthinate oils, fluid hydrates of oil of turpentine. There even appeared to be fluids present homologous with borneol, but (although higher in the series) having a lower boiling-point than borneol itself, and probably, therefore, isomeric with the borneol series. The substance was obtained from the fluid refusing to combine with the alkaline bisulphites. One fluid boiling at 191° contained,—

		C ²² H ²⁰ O ² requires
Carbon	78.7	78.6
Hydrogen	11.7	11.9
Oxygen	9.6	9.5
	100.0	100.0

Little attention was paid to these bodies, partly because they appeared to differ in different samples of oil, but chiefly because no positive guarantee of their purity could be obtained. The fact, however, was observed, that the above fluid, like borneol, yielded camphor when boiled with nitric acid.