

APPENDIX TO PAPER "ON ESSENTIAL OIL OF SAGE."

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Some Optical Properties of Constituents of Sage Oil.

MY best thanks are due to my friend, Mr. R. E. Day, M.A., of King's College, London, for his great kindness in making many measurements of the refractive indices of the constituents of sage oil.

The constituents of sage oil, separated as described in the preceding paper, cannot be regarded as pure; for this reason, and also because of the small quantities at my disposal, I have contented myself with determining only a few of the physical properties of these compounds; nor (while conducting these determinations with care) have I sought to carry out the measurements with extreme refinement.

In volume 12 of the *Berichte*, a paper appeared by Brühl (p. 2135), in which a formula is given for finding the true refraction coefficient (A) of a substance from determinations of the refractive indices for

two rays. By substituting A for μ in the ordinary formula, $\frac{\mu-1}{d}$, a constant is obtained for each substance, the value of which is independent of dispersion and temperature, and dependent only on the chemical structure of the substance examined. By multiplying this constant by the molecular weight of the substance, the *molecular refraction* is obtained.

The formulæ used for obtaining the value of A are as follows:—

$$\begin{aligned} \mu\lambda_1 &= A + \frac{B}{\lambda_1^2} & \text{Hence } B &= \frac{\mu\lambda_2 - \mu\lambda_1}{\frac{1}{\lambda_2^2} - \frac{1}{\lambda_1^2}} \\ \mu\lambda_2 &= A + \frac{B}{\lambda_2^2} & \text{and } A &= \mu\lambda_1 - \frac{B}{\lambda_1^2} \end{aligned}$$

where $\mu\lambda_1$ is the observed index for light of wave-length λ_1 , and $\mu\lambda_2$ the observed index for light of wave-length λ_2 .

In the following determinations the refractive indices were measured for the red hydrogen line, $H\alpha$, and for the violet line, $H\gamma$. Taking the wave-lengths of these lines as 3968 and 3933 respectively, we get

$$\frac{1}{\lambda_2^2} - \frac{1}{\lambda_1^2} = 0.000\,000\,03.$$

In calculating the molecular refractions of the compounds examined, I have used Brühl's numbers for the atomic refraction of carbon, hydrogen, and oxygen, viz., C = 4.86, H = 1.29, and O = 2.90.

Specific gravities are referred to water at the same temperature as that at which the determinations were made.

Sage Terpene, *b. p.* = 157°. *Separated from German Oil. (Dextrorotatory.)*—The data obtained were as follows. (Temp. = 15°):—

$$\mu H\alpha(\mu\lambda_1) = 1.4649. \quad \mu H\gamma(\mu\lambda_2) = 1.4755.$$

$$\text{Sp. gr. at } 15^\circ = 0.8635.$$

$$\text{Hence } \frac{A-1}{d}. M = 72.7; \text{ calculated} = 69.3; \text{ difference} = 3.4,$$

which is nearly equal to the mean difference obtained by Brühl for that class of carbon compounds containing two pairs of "doubly-linked" carbon atoms.

$C_{10}H_{16}$ *Hydrocarbon, boiling at about 170°. Separated from German Oil. (Dextrorotatory.)*—Temp. = 15°.

$$\mu H\alpha = 1.4635. \quad \mu H\gamma = 1.4755. \quad \text{Mean value of } \mu = 1.4695.$$

$$\text{Sp. gr. at } 15^\circ = 0.8653.$$

$$\text{Taking the mean value of } \mu \text{ we get } \frac{\mu-1}{d}. \text{ Mean} = 73.8.$$

$C_{10}H_{16}$ *Hydrocarbon, boiling about 170°. Separated from English Oil.*

(*slightly lævorotatory*.)—Mean value of $\mu = 1.4698$ (15°). Sp. gr. at $15^\circ = 0.8667$. Hence $\frac{\mu - 1}{d} \cdot M = 73.7$.

As I cannot be certain of the purity of this hydrocarbon (see paper on "Sage Oil," par. 6), I have not applied Brühl's formula. The value of $\frac{\mu - 1}{d} \cdot M$ is constant, whether the data be those obtained for the hydrocarbon from German, or for that from English oil; the difference between this and the calculated value is about equal to the difference observed in the case of sage terpene.

Terpene distilled in 1876, and redistilled in 1879 (see paper, par. 4). (15° .)

$$\mu_{H\alpha} = 1.4658. \quad \mu_{H\gamma} = 1.4796. \quad \text{Mean value of } \mu = 1.4727.$$

Taking the former sp. gr. (0.8635), we have $\frac{\mu - 1}{d} \cdot M = 74.3$ which is nearly the same as the value obtained for the freshly distilled terpene. This terpene was lævorotatory; it was also lævorotatory in 1876.

Salviol, b. p. = 200°. Separated from German Oil. (Dextrorotatory.) (15° .)

$$\mu_{H\alpha} = 1.4559. \quad \mu_{H\gamma} = 1.4733. \quad \text{Sp. gr. at } 15^\circ = 0.938.$$

Hence $\frac{A - 1}{d} \cdot M = 74.2$; calculated = 74.7. Hence by Brühl's rule salviol contains no "doubly linked" pairs of carbon-atoms.

Cedrene boiling about 260°. Separated from German oil. (Inactive.) (15° .)

$$\mu_{H\alpha} = 1.4996. \quad \mu_{H\lambda} = 1.5147. \quad \text{Mean value of } \mu = 1.5071.$$

Cedrene separated from first sample of English oil. Mean value of μ at $15^\circ = 1.4979$. The same number was obtained for the cedrene separated from the second sample of English oil. Hence mean value of μ for all cedrenes = 1.5025. Mean sp. gr. at $15^\circ = 0.915$.* As none of the cedrenes are quite free from other liquids, I have simply calculated the value of $\frac{\mu - 1}{d} \cdot M$, and find it to be = 111.9; calculated = 103.9; difference = 8.0; which by Brühl's rule shows four pairs of "doubly linked" carbon-atoms in sage cedrene.

If there be in sage oil an isomeride of terpene, boiling at about 170° , these results show that it probably belongs to the same type of $C_{10}H_{16}$

* From the data given in a former paper (Sigiura and Muir, this Journal [1], 1878, 278), the value of d at 15° for cedrene from English oil is found to be = 0.912. The value of d as directly determined for the cedrene from German oil was = 0.918 (15°). Hence the mean specific gravity of sage cedrene at 15° is = 0.915.

hydrocarbons as terpene itself, *i.e.*, to the type containing two pairs of "doubly linked" carbon-atoms; whilst on the other hand salviol appears to have all its carbon atoms "singly linked." If the formulæ given by Armstrong for terpene and camphor (*Ber.*, **12**, 1698) be adopted,* we should have the $C_{10}H_{16}$ hydrocarbon of sage classed with those of citron oil, orange oil, &c., whilst salviol must be closely allied to camphor. The passage from this hydrocarbon to salviol appears to be attended with a loosening of the double links of the two pairs of carbon-atoms; but at the same time the polymerisation of the $C_{10}H_{16}$ to $C_{15}H_{24}$ is accompanied by a further process of "double linking." In the paper on sage oil reasons have been given in favour of regarding the oxidation, hydration, and polymerisation of $C_{10}H_{16}$ hydrocarbons as simultaneously occurring changes.

I have sought to apply Brühl's formula to the data obtained by other observers for a few oxidised oils, and for cedrene (see especially Gladstone, this Journal [2], **10**, 1; and this Journal, **11**, 972); but the results (a few of which are annexed) seem to indicate that these oils have not been free from impurities when their refractive indices were determined.

Difference between observed and
calculated values for

$$\left(\frac{A-1}{d}\right) \cdot M.$$

Citronellol, $C_{10}H_{18}O$	4·8
Cajeputol, $C_{10}H_{18}O$	1·5
Myristicol, $C_{10}H_{16}O$	3·4
Absinthol, $C_{10}H_{16}O$	3·3

In the hydrocarbons of the formula $C_{15}H_{24}$, the value of the difference varies from 4·4 to 7·0.
