

whether the N-ethyl quinazolone would be formed and ethyl iodide split off<sup>1</sup>, but no such change occurred.

*Ethylation of 5-nitro-2-ethyl-4-hydroxyquinazoline.*—When the alkylation was carried out at atmospheric pressure, good crystals were obtained, melting sharply at 148-149°, which proved to be the ethoxy compound. On recrystallization from alcohol, they were rearranged completely to the N-ethyl isomer (m. p. 180°-181°). The product from the sealed tubes melted at 166°-167°, and was a mixture of the —OR and —NR isomers, for on recrystallization from alcohol it gave the pure oxygen ether. That this was due to a rearrangement and not to a fractional crystallization seems clear from the fact that there was no loss in the weight of the crystalline material separated and there were no other products in the mother-liquor. This oxygen ether is, therefore, less stable than its methyl homologue.

Nitrogen found, 17.14 and 16.98. Calculated for  $C_{12}H_{15}O_3N_3$ : N, 17.00.

*Ethylation of 7-nitro-2-methyl-4-hydroxyquinazoline* gave similar results. The reaction was conducted at ordinary pressure and the only products were the oxygen ether and unchanged quinazoline. The oxygen ether melts at 105°-106° (cor.), while the isomeric N-ethyl compound has a melting-point of 175° (cor.). Recrystallized from alcohol, it showed no inclination to pass into its isomer, resembling in this respect the corresponding 5-nitro compound.

Nitrogen found, 17.95. Calculated for  $C_{11}H_{11}O_3N_3$ : N, 18.00.

### 3. Amylation.

*Amylation of 7-nitro-2-methyl-4-hydroxyquinazoline.*—The experiments were conducted both at ordinary pressure and in sealed tubes at 150°. Ethyl alcohol was used as the solvent. In all cases the chief products were the oxygen ether and unchanged quinazoline. The latter was easily removed by washing with dilute alkali. The pure isoamyloxy compound forms large, flat plates, which melt at 104° (cor.), and no rearrangement is effected by boiling alcohol.

Nitrogen found, 15.41. Calculated for  $C_{14}H_{17}O_3N_3$ : N, 15.27.

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## ON THE PRINCIPLE OF OPTICAL SUPERPOSITION. II

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In my first paper on the subject<sup>2</sup> I showed that the universally accepted

<sup>1</sup> Compare Knorr; *Ann.*, 236, 87, (1887).

<sup>2</sup> This Journal, 28, 525 (1906); *Z. physik. Chem.*, 56, 565 (1906.) To the bibliography mentioned in that paper should be added: Percy Frankland and Price, *J. Chem. Soc.*, 1897, 266-268.

principle of optical superposition is probably erroneous and that our present knowledge concerning the rotatory power of asymmetric carbon atoms is summed up by the following law:

*"The optical rotatory power of an asymmetric carbon atom depends upon the composition, constitution, and configuration of each of its four groups."*

As I have pointed out before, the data really capable of throwing light on the much misunderstood question of optical superposition are very scarce. The new experimental material that I expect to furnish is not yet available. Meanwhile, I will, in the present paper, offer what seems to me an important addition to the material presented in my first communication.

Guye and Goudet<sup>1</sup> have studied optical superposition in the interesting case of the diamyl esters of divaleryl-tartaric acids, which contain six asymmetric carbon atoms. Their figures are as follows:

<i>l</i> -amyl <i>dl</i> -valeryl- <i>dl</i> -tartrate <sup>2</sup>	$[\alpha]_D$
<i>dl</i> - " <i>d</i> - " <i>-dl</i> - "	+ 2.44°
<i>dl</i> - " <i>dl</i> - " <i>-d</i> - "	+ 3.48°
	+ 6.42°
Sum,	+ 12.34°

On the other hand, a direct determination gave:

$$l\text{-amyl } d\text{-valeryl-}d\text{-tartrate } [\alpha]_D = 11.32^\circ.$$

The agreement might at first sight be considered as "just about sufficient." Closer study, however, reveals the fact that there is no agreement at all and that the observation furnishes strong evidence against the assumption of algebraic superposition and in favor of the principle which I have proposed in its place.

Considering the first three observations consecutively, we find that in the first one a 1 dm. tube was filled with *l*-amyl *dl*-valeryl-*dl*-tartrate. This however, was obviously not a single substance, but a mixture of the following compounds:

- (1) *l*-amyl *d*-valeryl-*d*-tartrate
- (2) *l*- " *d*- " *-l*- "
- (3) *l*- " *l*- " *-d*- "
- (4) *l*- " *l*- " *-l*- "

Similarly, the *dl*-amyl *d*-valeryl-*dl*-tartrate had the following composition:

- (5) *d*-amyl *d*-valeryl-*d*-tartrate
- (6) *l*- " *d*- " *-d*- "
- (7) *d*- " *d*- " *-l*- "
- (8) *l*- " *d*- " *-l*- "

<sup>1</sup> C. R. 122, 932 (1896).

<sup>2</sup> *dl* stands for *racemic*. See Fischer, Ber. 40, 102 (1906).

Finally, the *dl*-amyl *dl*-valeryl-*d*-tartrate contained:

- (9) *d*-amyl *d*-valeryl-*d*-tartrate
- (10) *d*- " *l*- " *d*- "
- (11) *l*- " *d*- " *d*- "
- (12) *l*- " *l*- " *d*- "

Each of these ingredients may be thought of as occupying one-quarter of a 1 dm. tube. And since the antipodal couples 2 and 10, 3 and 7, 4 and 5, have no rotatory power at all, the algebraic sum of the rotations of the twelve substances was really due to the following quantities:

- (a)  $\frac{3}{4}$  of a 1 dm. tube full of *l*-amyl *d*-valeryl-*d*-tartrate (Nos. 1, 6, and 11);
- (b)  $\frac{1}{4}$  of a 1 dm. tube full of *l*-amyl *d*-valeryl-*l*-tartrate (No. 8);
- (c)  $\frac{1}{4}$  of a 1 dm. tube full of *d*-amyl *d*-valeryl-*d*-tartrate (No. 9);
- (d)  $\frac{1}{4}$  of a 1 dm. tube full of *l*-amyl *l*-valeryl-*d*-tartrate (No. 12).

The sum of the rotations of *a*, *b*, *c*, and *d* is compared with the rotation of a 1 dm. tube full of *l*-amyl *d*-valeryl-*d*-tartrate. This latter substance gave  $[\alpha]_D = 11.32^\circ$ . Three-fourths of a 1 dm. tube full of it would give  $11.32^\circ \times \frac{3}{4} = 8.49^\circ$ . A number of Guye's and Walden's results show that the influence of racemic mixtures present as solvents amounts on an average to  $\pm 0.28^\circ$  PER 1 DM. TUBE (*Nota bene!*), or  $\pm 0.21^\circ$  per three quarters of a 1 dm. tube. Adding<sup>1</sup> this to  $8.49^\circ$ , we get  $8.70^\circ$  as the rotation due to *a*. And subtracting this from  $12.34^\circ$  (the total rotation produced by *a*, *b*, *c*, and *d*), we get  $3.64^\circ$  as the rotation due to *b*, *c*, and *d*.

To recapitulate briefly: The rotation due to substances Nos. 1 to 12 should be equal to the rotation of a 1 dm. tube full of *l*-amyl *d*-valeryl-*d*-tartrate. The rotation due to Nos. 2, 10, 3, 7, 4, 5, 6, and 11 together, which is practically identical with the rotation of  $\frac{3}{4}$  of a 1 dm. tube full of *l*-amyl *d*-valeryl-*d*-tartrate, is calculated to be  $8.70^\circ$ . This leaves a rotation  $3.64^\circ$  for Nos. 8, 9, and 12 together.

Now, if the principle of optical superposition were correct, *this last-named rotation should be equal to that produced by  $\frac{1}{4}$  of a 1 dm. tube full of l-amyl d-valeryl-d-tartrate.* (The rotation of the other ingredients has no bearing at all on the principle of superposition). But in order to employ the quantity always used for such comparisons, namely, not one-quarter, but *one* decimeter tube, we multiply the  $3.64$  by 4 and get  $14.56^\circ$ .

We thus have:

- I. Rotation due to a mixture which according to the principle of superposition, should be equal to that of a 1 dm. tube full of *l*-amyl *d*-valeryl-*d*-tartrate  $14.56^\circ$

<sup>1</sup> The probabilities that the required correction is positive or negative are even. I add  $0.21^\circ$  in order to show that even under the most favorable assumption the experiments under discussion contradict the Principle of Superposition definitely (See further below).

II. Actual rotation of a 1 dm. tube full of *l*-amyl *d*-valeryl-*d*-tartrate  
11.32°

The difference per 1 dm. tube is thus 3.24°. In comparison with the usual difference, in such cases, of about 0.28° per 1 dm. due to the purely physical influence for solvents, a difference of 3.24° is enormous<sup>1</sup>.

The conclusion is plain: The principle of optical superposition is false, and the principle I have formulated must take its place.

NEW YORK UNIVERSITY,  
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THE ESSENTIAL OIL OF THE PACIFIC ARBOR VITÆ.

BY W. C. BLASDALE.

Received January 23, 1907.

The Pacific arbor vitæ (*Thuya plicata*), which is known locally under the name of red or canoe cedar, bears a close resemblance to its better known eastern analogue (*Thuya occidentalis*), the so-called white or swamp cedar, but attains a much greater size than the latter, and differs from it in its habit of growth and in a number of minor characters. It forms one of the most important constituents of the dense forests of Eastern Washington and Oregon, and at the present time is being cut in enormous quantities for the manufacture of shingles, for which purpose the unusual durability of the wood renders it especially valuable.

An essential oil derived from the eastern species of arbor vitæ is an article of commerce, though sold under the name of Oil of Cedar Leaves. The present supply is produced in Eastern Vermont and in Maine and is used in the preparation of ointments, as an insecticide and in the composition of certain liniments used as a remedy for rheumatism. It has been examined by Jahn<sup>2</sup>, Wallach<sup>3</sup> and Semmler<sup>4</sup> and its important constituents found to be *d*-pinene, *l*-fenchone, *d*-thuyone, and probably inactive carvacrol. No examination of the chemical constituents of the Pacific arbor vitæ appears to have been made and the writer availed himself of an opportunity afforded while acting as Collaborator of the Bureau of Forestry some years ago to secure sufficient material for a preliminary study of it.

About 13.8 kilos of the air-dry foliage were distilled with steam till the distillate was no longer turbid. On standing a dark brown oil separated, the total amount being about 400 cc. The oil possesses a penetrating terpene-like odor. Determination of the physical constants gave the following results:—

<sup>1</sup> Had the correcting 0.21° been subtracted instead of being added in the above calculation as might have been done with equal right, the final difference would have come out even greater: nearly 5° per 1 dm. tube.

<sup>2</sup> Jahn. Chem. Centr., 1884, 39.

<sup>3</sup> Wallach, Ann., 272, 99; 275, 179.

<sup>4</sup> Semmler, Ber., 25, 3343.