

THE INFLUENCE OF CERTAIN GROUPS ON ROTATORY POWER.

(TRANSLATED FROM THE GERMAN.)

Professor Dr. H. Rupe (Basle) read a Paper on "The Influence of Certain Groups on Rotatory Power."

My earlier experiments on the relation between constitution and optical activity were made with the menthyl esters of various acids; more recently, I have worked with derivatives of citronellal, of carvoxime, myrtenol, and methylene-camphor. One of my English colleagues has pointed out that we cannot expect clear answers to our questions except by using optically active compounds with only one asymmetric carbon atom, and that these must be liquid and give liquid compounds, so that no solvent is necessary.* But this is an ideal we are not able to attain in every case. Moreover, the same author has pointed out in a recent paper † that the influence of homologous groups on optical rotatory power is sometimes developed in a more striking way in solution than when no solvent is used. Again, whilst it is a most desirable thing to work with compounds containing only one asymmetric carbon atom, the influence on rotatory power of several asymmetric carbon atoms in one molecule is as yet very little understood. I have made a comparative table of corresponding series of compounds with one, two, and three asymmetric carbons, but have not been able to come to any conclusion about it, the material being as yet not sufficient. At the present time I am in agreement with Hilditch, when he says that the number of asymmetric atoms in a given molecule has little bearing upon the changes of rotatory power produced by constitutive influences. Here, indeed, we find a subject for future researches.

Influence of Alkyl Groups on Rotatory Power.

The change of rotatory power produced by the introduction of an alkyl group into a saturated or unsaturated chain (replacement of a hydrogen atom in $\cdot\text{CH}_3$, $:\text{CH}_2$, or $:\text{CH}$) is usually insignificant; this was found to be the case, for instance, when a methyl group was introduced into the molecule of a saturated or unsaturated fatty acid, a phenylated acid, citronellal, carvoxime, or methylene-camphor. Several exceptions were indeed observed, but a special explanation can be given in almost every case. We are therefore entitled to state, as a general proposition, that the optical influence of saturated alkyl groups is a small one. ‡

* Pickard and Kenyon, *Trans. Chem. Soc.*, **99**, 45 (1911).

† *Ibid.*, **103**, 1923 (1913).

‡ The branching of the carbon-chain of an alkyl group sometimes has a remarkable effect (Pickard and Kenyon, *Trans. Chem. Soc.*, **99**, 45 (1911); E. Fischer, *Ber.*, **42**, 2981).

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Some authors* are of opinion that the accumulation of identical radicals upon a carbon atom near the asymmetric atom produces a kind of symmetry, which results in a diminution of rotatory power. I have studied this question with Ahner and wish now to draw your attention to the fact that, whilst the specific rotatory power of the substituted acetic esters diminishes a little from monomethyl- to trimethyl-acetic acid, the molecular rotatory power

TABLE I.

Menthyl-ester of	$[\alpha]_D$	M_D
$\text{CH}_3 \cdot \text{CH}_2 \cdot \text{COOH}$	75.51	160.2
$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \text{ > CH} \cdot \text{COOH}$	72.05	163.5
$\begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \\ \text{CH}_3 \end{array} \text{ > CH} \cdot \text{COOH}$	67.3	161.5

is practically constant. The symmetry of the trimethylacetic acid has therefore no marked influence on the asymmetric system (Table I).

Influence of Unsaturated Groups on Optical Rotatory Power.

Before dealing with this matter, I am glad to say that I agree in every point with Professor Frankland,† when he says: "The presence of unsaturation leads to an irregularity in the rotatory effect, and not necessarily to an increased rotation." To discover some law in these irregularities, to study those often contradictory facts, seems to me to be one of the most attractive problems of our science. It is well known that a double linking between two carbon atoms, in a position near the asymmetric carbon, has sometimes a powerful effect. If I am not mistaken, this was discovered by Walden.‡ In 1903 the great influence of Thiele's "conjugated" double bonds was discovered from experiments on the menthyl ester of sorbic acid, $\text{CH}_3 \cdot \text{CH} : \text{CH} \cdot \text{CH} : \text{CH} : \text{CO}_2\text{R}$.§ As time is too short to describe all the interesting researches that have been made in England on the influence of unsaturation on rotatory power, I will draw your attention exclusively to the effect of this conjugation.

Conjugation of Unsaturated Groups.

There are three different kinds of conjugation, which have all been well studied. I will begin with the simple conjugated double bonds between carbon atoms only, without any phenyl group. Data have been provided by the study of the menthyl-esters of sorbic acid and its reduction-products. In cinnamyl-acrylic acid we have, of course, a second conjugation with the

* *Zeitschr. f. physik. Chem.*, **77**, 482 (1911).

† Frankland, *Trans. Chem. Soc.*, **101**, 661 (1912).

‡ Walden, *Zeitschr. f. physik. Chem.*, **20**, 569 (1896).

§ Rupe, *Ann.*, **372**, 167 (1903).

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phenyl group, but both vanish in phenyl-pentenic acid. But here we very soon meet with a curious fact, the anomaly represented by dimethylsorbic acid—

TABLE II.

	[α] _D .
<i>Menthyl-esters of Sorbic Acid and its Reduction-products.</i>	
CH ₃ · CH : CH · CH : CH · CO · O · C ₁₀ H ₁₉	88·53
CH ₃ · CH ₂ · CH : CH · CH ₂ · CO · O · C ₁₀ H ₁₉	65·11
CH ₃ · CH ₂ · CH ₂ · CH ₂ · CH ₂ · CO · O · C ₁₀ H ₁₉	64·86
<i>Menthyl-esters of Cinnamyl-acrylic Acid and its Reduction-products.*</i>	
C ₆ H ₅ · CH : CH · CH : CH · CO · O · C ₁₀ H ₁₉	75·14
C ₆ H ₅ · CH ₂ · CH : CH · CH ₂ · CO · O · C ₁₀ H ₁₉	47·54
C ₆ H ₅ · CH ₂ · CH ₂ · CH ₂ · CH ₂ · CO · O · C ₁₀ H ₁₉	33·86
<i>Menthyl-esters of Dimethylsorbic Acid and its Reduction-products.†</i>	
CH ₃ · C : CH · C : CH · CO · O · C ₁₀ H ₁₉	59·80
CH ₃ CH ₃	
CH ₃ · CH · CH : C · CH ₂ · CO · O · C ₁₀ H ₁₉	68·51
CH ₃ CH ₃	
CH ₃ · CH · CH ₂ · CH · CH ₂ · CO · O · C ₁₀ H ₁₉	57·38
CH ₃ CH ₃	

Looking for an explanation I was quite helpless for a couple of years, until Auwers and Eisenlohr discovered the very remarkable fact that the influence of conjugation on refraction is much disturbed by alkyl groups, connected with the double linkings, which may entirely destroy the optical exaltation which is observed in normal cases. There is a marked resemblance between Auwers' formulæ and that of the dimethylsorbic acid. In each case we have methyl groups, connected with the central carbons of the double bonds, exerting a powerful effect on the conjugation. I admit that this is no explanation, but at least we find here a remarkable analogy.

Frankland and O'Sullivan † found that allyl and propyl derivatives frequently have the same optical rotatory power ; at least, the difference between the two is small, sometimes the former and sometimes the latter having the greater effect. I made the same observation in some experiments with Lenzinger § on the influence of the introduction of the allyl group in the menthyl esters of aceto-acetic acid and benzoyl-acetic acid. The rotatory

* Rupe and Münter, *Ann.*, **369**, 330 (1909).

† Rupe and Lotz, *Ann.*, **369**, 344 (1909).

‡ Frankland and O'Sullivan, *Trans. Chem. Soc.*, **99**, 2325 (1911).

§ Rupe and Lenzinger, *Ann.*, **395**, 135 (1912).

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power of the menthyl ester was not at all remarkable, the unsaturated complex being too far away from the asymmetric carbon ; but when the double-bond of the allyl group is allowed to enter, in combination with a second one, so that a conjugation may be formed, we have again a strong optical effect. This rule is well demonstrated by the two compounds of citronellal, prepared by Jäger * from allylbromide and propylbromide in presence of magnesium. The conjugation here is nearer to the asymmetric carbon atom than in the above examples.

TABLE III.

	[α] _D .	M _D .	
CH ₃ ·CO·CH·CO ₂ H · · · CH ₂ ·CH ₂ ·CH ₃	57·27	161·6	Menthyl-esters of allyl- and propyl-derivatives of aceto-acetic and benzoyl-acetic acids.
CH ₃ ·CO·CH·CO ₂ H · · · CH ₂ ·CH : CH ₂	58·27	163·3	
CH ₃ ·CO·CH·CO ₂ H · · · CH ₂ ·CH : CH·C ₆ H ₅	41·31	147·2	
C ₆ H ₅ ·CO·CH·CO ₂ H · · · CH ₂ ·CH ₂ ·CH ₃	52·35	180·2	
C ₆ H ₅ ·CO·CH·CO ₂ H · · · CH ₂ ·CH : CH ₂	51·40	175·9	
C ₆ H ₁₁ ·CH·CH ₂ ·CH : CH·CH ₂ ·CH ₃ ... · · CH ₃	6·68	9·40	Derivates prepared from citronellal.
C ₆ H ₁₁ ·CH·CH ₂ ·CH : CH·CH : CH ₂ ... · · CH ₃	10·12	18·03	

Influence of a Phenyl Group on Rotatory Power.

Very curious is the effect of a phenyl group and not easy to analyse. Close to the asymmetric carbon atom it nearly always increases the optical rotation. But here already we find some exceptions. Thus the benzoate of carboxime † has a lower rotation than the phenylacetate and phenylpropionate. When the phenyl-group is displaced away from the asymmetric carbon atom, its positive increasing effect diminishes, until it becomes less than that of an alkyl-group. Finally, the effect may even become negative.

What is the reason of this phenomenon? There was a time when I thought that it might be the effect of a lever, that the influence of the phenyl group actually increased with its distance from the asymmetric carbon atom. I hoped to find Guye's well-known hypothesis in a new form. That may be correct, but it is necessary to be very cautious in this matter and to avoid drawing conclusions prematurely.

* Rupe and Jäger, *Ann.*, **402**, 149 (1913).† Rupe and Wolfsleben, *Ann.*, **395**, 136 (1912).

TABLE IV.

	[α] _D .	M _D .	
CH ₃ · CO · O · C ₁₀ H ₁₉	73·77	146·2	
C ₆ H ₅ · CO · O · C ₁₀ H ₁₉	90·90	236·5	
CH ₃ · CH ₂ · CO · O · C ₁₀ H ₁₉	75·51	160·2	
C ₆ H ₅ · CH ₂ · CO · O · C ₁₀ H ₁₉	67·57	185·0	
CH ₃ · CH ₂ · CH ₂ · CO · O · C ₁₀ H ₁₉	70·46	159·6	
C ₆ H ₅ · CH ₂ · CH ₂ · CO · O · C ₁₀ H ₁₉	58·48	186	
CH ₃ · CH ₂ · CH ₂ · CH ₂ · CO · O · C ₁₀ H ₁₉	64·86	164·9	
C ₆ H ₅ · CH ₂ · CH ₂ · CH ₂ · CO · O · C ₁₀ H ₁₉	33·86	107·0	
Carvoxime {	C ₁₀ H ₁₄ NO · CO · C ₆ H ₅	11·56	31·09
	C ₁₀ H ₁₄ NO · CO · CH ₂ · C ₆ H ₅	27·47	77·74
	C ₁₀ H ₁₄ NO · CO · CH ₂ · CH ₂ · C ₆ H ₅	77·23	77·90

Time does not permit me to give a full account of the work that has already been commenced in our laboratory, but here is a little contribution to this matter. When we compare the menthyl esters of the three acids: propionic acid, phenylacetic acid and hexahydrophenylacetic acid, the latter should have the greatest influence in diminishing the optical rotation, for there we have the heaviest mass at the end of the lever.

TABLE V.

	[α] _D .
Menthyl-ester of propionic acid, CH ₃ · CH ₂ · CO · O · C ₁₀ H ₁₉ ...	- 75·51
Menthyl-ester of phenylacetic acid, C ₆ H ₅ · CH ₂ · CO · O · C ₁₀ H ₁₉ ...	- 67·57
Menthyl-ester of cyclohexylacetic acid, C ₆ H ₁₁ · CH ₂ · CO · O · C ₁₀ H ₁₉ ...	- 57·15

Experiments made in conjunction with Hoerder have shown that this is in fact what happens, the hexahydro-compound possessing the smallest rotatory power. But I will not insist on this fact, because the group C₆H₁₁, the radical of cyclohexane, has itself but little influence on the asymmetric carbon. In spite of its big mass and volume, its influence is not greater than the effect of an alkyl group, and is sometimes even smaller.

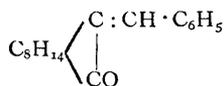
Specific and Molecular Rotation.

May I be allowed at this point to make a remark on specific and molecular rotation, which will, I feel sure, meet with some opposition? I agree that

molecular rotation is of the greatest value when we have to deal with homologous series (especially in aliphatic compounds). But when we replace, for instance, a methyl by a phenyl group, and thus pass from an inert alkyl group to an unsaturated group, with a large volume and much residual affinity, we should consider in the first place not the molecular rotation but the specific rotation; for if we think to eliminate the molecular weight by multiplying the specific rotation by the latter, we attribute too great an influence to this factor. Many subtle changes of constitution are indicated at once by variations of specific rotation where the molecular rotation leaves us in the lurch!*

Conjugation of the Phenyl Group with a Double Linking.

This combination has in every case a very marked influence on the optical rotation, especially when the conjugated group is close to the asymmetric atom. A few examples of the great amount of work done on this subject may be given. We have the interesting discoveries of Haller † in the camphor series, showing an enormous elevation of the rotation in benzylidene-camphor—



The rotatory power diminishes greatly when we exchange the phenyl group for the cyclohexyl-radical or the benzyl group, where we have no conjugation. Other examples are given (I) by the phenyl-derivative from citronellal and phenylmagnesiumbromide, ‡ by the corresponding cyclohexyl-compound, (II) by the hydrogen camphorates of eugenol and iso-eugenol, (III) discovered by Hilditch, § by cinnamylidenecamphor and phenylpropionylcamphor, || (IV) by the optically-active esters of cinnamic acid and hydrocinnamic acid, ¶ (V) the diacetyl- and the dibenzoyl-ethyl-tartrate, ** (VI) the (above-mentioned) allyl- and propyl-derivative (VII) prepared by the reaction of allyl- and propyl-magnesium bromide with citronellal. ††

In his paper of the year 1909, †† on the effect of contiguous unsaturated groups on optical activity, Hilditch expresses the opinion that the influence of unsaturated groups depends at least as much on the proximity of the unsaturated nucleus to a carboxyl group as to the asymmetric system, or, in other words, on the degree of conjugation together with the nearness of the entire conjugated system to the asymmetric part of the molecule. Smiles, in his book of chemical constitution and physical properties, goes further when he quotes Hilditch, and says that the effect of unsaturated groups depends only on conjugation, and not at all on distance. On this point I am sorry to differ from my English colleagues!

More than ever, I am to-day of the opinion that the influence of a conjugation, or of any other group which largely increases or diminishes the rotatory power, is a function of its distance from the asymmetric carbon atom.

* Rupe, *Ann.*, **395**, 129 (1912).

† Haller, *Compt. rend.*, **136**, 1222 (1903).

‡ Rupe and Jäger, *Ann.*, **402**, 149 (1913).

§ Hilditch, *Trans. Chem. Soc.*, **97**, 223 (1910).

|| Rupe and Frisell, *Ber.*, **38**, 104 (1905).

¶ Rupe and Busolt, *Ann.*, **369**, 356 (1909).

** Hilditch, *Trans. Chem. Soc.*, **99**, 224 (1911).

†† Rupe and Jäger, *Ann.*, **402**, 171 (1913).

‡‡ Hilditch, *Trans. Chem. Soc.*, **93**, 1, 700, 1338, 1618 (1908); **95**, 289, 331, 1570, 1579 (1908); **97**, 223, 1091, 2110 (1910); **99**, 218, 224 (1911).

TABLE VI.

	$[\alpha]_D$.	M_D .
I		
$C_8H_{14} \begin{cases} C:CH \cdot C_6H_5 \\ \\ C:O \end{cases}$	429'25	1020
$C_8H_{14} \begin{cases} C:CH \cdot C_6H_{11} \\ \\ C:O \end{cases}$	—	323
$C_8H_{14} \begin{cases} CH \cdot CH_2 \cdot C_6H_5 \\ \\ CO \end{cases}$	—	248
II		
$C_6H_{11} \cdot CH(CH_3) \cdot CH:CH \cdot C_6H_5 \dots$	63'24	135'4
$C_6H_{11} \cdot CH(CH_3) \cdot CH_2 \cdot CH_2 \cdot C_6H_5$	7'62	
III		
$C_8H_{14}(CO_2H) \cdot CO_2 \cdot C_6H_4 \cdot CH:CH \cdot CH_3$...	38'6	
$C_8H_{14}(CO_2H) \cdot CO_2 \cdot C_6H_4 \cdot CH_2 \cdot CH:CH_2$...	32'7	
IV		
$C_8H_{14} \begin{cases} C:CH \cdot CH:CH \cdot C_6H_5 \\ \\ C:O \end{cases}$	296'11	
$C_8H_{14} \begin{cases} CH \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot C_6H_5 \\ \\ C:O \end{cases}$	66'35	
V		
$C_6H_5 \cdot CH:CH \cdot CO_2H$	76'95	220'8
$C_6H_5 \cdot CH_2 \cdot CH_2 \cdot CO_2H$	58'48	168'4
VI		
$CH_3 \cdot CO \cdot O \cdot CH \cdot CO_2C_2H_5$	—	9'9
$CH_3 \cdot CO \cdot O \cdot \begin{matrix} \\ CH \cdot CO_2C_2H_5 \end{matrix}$		
$C_6H_5 \cdot CO \cdot O \cdot CH \cdot CO_2C_2H_5$	—	247'1
$C_6H_5 \cdot CO \cdot O \cdot \begin{matrix} \\ CH \cdot CO_2C_2H_5 \end{matrix}$		
VII		
$C_6H_{11} \cdot CH(CH_3) \cdot CH_2 \cdot CH:CH \cdot CH:CH_2$...	10'12	18'03
$C_6H_{11} \cdot CH(CH_3) \cdot CH_2 \cdot CH:CH \cdot CH_2 \cdot CH_3$...	6'68	12'03

I am now working, with my assistant, on this subject. In a recent paper we were able to show that the phenyl-derivative, which Klages* prepared from citronellal and which we also studied,† has a strong exalting effect on the rotatory power, the conjugation being very near to the asymmetric atom. If now we displace the same conjugation a little further, the effect is marvellous! We see an extremely strong depression of the rotation.

TABLE VII.

	$[\alpha]_D$.	M_D .
$C_6H_{11} \cdot CH(CH_3) \cdot CH : CH \cdot C_6H_5 \dots \dots \dots$	63.24	135.4
$C_6H_{11} \cdot CH(CH_3) \cdot CH_2 \cdot CH : CH \cdot C_6H_5 \dots \dots \dots$	3.33	7.60

That the influence of a conjugation is a function of its distance from the asymmetric carbon atom is further demonstrated by the menthyl-esters of the α - and β -phenyl-cinnamic acid.‡

TABLE VIII.

	$[\alpha]_D$.	M_D .
$C_6H_5 \cdot CH : C(C_6H_5) \cdot CO_2H \dots \dots \dots$	53.44	193.4
$C_6H_5 \cdot C(C_6H_5) : CH \cdot CO_2H \dots \dots \dots$	37.92	137.4

Both acids contain a conjugation, but in the second acid this conjugation is remote from the asymmetric carbon atom.

It is Hilditch's § merit that he directed attention to the influence of the carbonyl or ketonic group, which, as he proved, can very often enter into conjugation with an ethenoid group, thus producing an increased optical rotation. A very strong combination indeed is the benzene nucleus combined with the carbonyl-carboxyl group— $CO \cdot CO \cdot O$ —and so forth. He regards the influence of the CO group as equivalent to the ethenoid group, or perhaps somewhat less; the combination of the carbonyl with the carboxyl group exerts an influence comparable to that displayed by a benzoyl radicle.||

It may be useful to consider data for the derivatives of menthyl acetoacetate and menthyl benzoylacetate.¶ Here also we see the very peculiar effect of distance (Table IX.); we remark how little is the influence of the various conjugations of the ketonic and the phenyl group. The conjugation of the phenyl group with the double linking is so far away from the asymmetric carbon atom that it has but little influence of the rotatory power.

* Klages and Santter, *Ber.*, **39**, 1939 (1906).

† Rupe and Jäger, *Ann.*, **402**, 179 (1913).

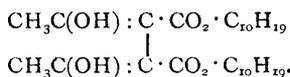
‡ Rupe and Busolt, *Ann.*, **369**, 311 (1909).

§ Hilditch, *Trans. Chem. Soc.*, **99**, 224 (1911).

|| The strong influence of a CO group has already been pointed out by Rupe and Frisell, *Ber.*, **38**, 106 (1905).

¶ Rupe and Lenzing, *Ann.*, **395**, 87 (1912).

108·82°, reaching a maximum in the course of ten minutes. This further change is, perhaps, due to the formation of a second enolic group :



Accumulation of Unsaturated Groups.

An unsaturated group has not always an exalting influence on the rotatory power, but very often produces the opposite effect. We nearly always observe a depression of the rotation when such a group is remote from the asymmetric carbon atom, but the same effect is often seen when it is near the active complex, especially when there happens to be, what I called in a paper published some years ago,* an accumulation of unsaturated groups, as, for instance, a benzene nucleus combined with a double linking, a conjugated double bond, a ketonic or a second phenyl-group.

A considerable amount of work has already been done on this subject. α - and β -phenylcinnamic acids both have a lower rotatory power than the corresponding saturated acids.† In the β -phenylcinnamic acid, where we find a heavy accumulation of unsaturated groups, we meet with one of the smallest rotations ever found in a menthyl ester. The corresponding saturated acid produces a much greater optical rotation. Moreover, we see, with one slight exception, that whenever a phenyl group enters an unsaturated chain, the specific rotation, and nearly always the molecular rotation, diminishes in comparison with the rotation produced by the corresponding methyl-compound.

TABLE X.

	$[\alpha]_D$.	M_D .	
$\text{C}_6\text{H}_{11} \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{C}_6\text{H}_5 \dots$	3·3	7·6	Hydrocarbons from citronellal. ‡
$\text{C}_6\text{H}_{11} \cdot \text{CH}(\text{CH}_3) \cdot \text{CH}_2 \cdot \text{CH} : \text{CH} \cdot \text{CH}_3 \dots$	6·6	11·0	
$\text{C}_9\text{H}_{14}\text{O} \cdot \text{C} : \text{CH} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5 \dots \dots$	129·0	327·6	Derivatives of methylene- camphor.§
$\text{C}_9\text{H}_{14} \cdot \text{O} \cdot \text{C} : \text{CH} \cdot \text{CH}_2 \cdot \text{CH}_3 \dots \dots$	172·85	332·1	

In a recent paper by McKenzie and Martin|| there is a remarkable contribution to the effect on the rotatory power of an accumulation of unsaturated groups.

When we examine the effect of substituting a methyl for a phenyl group in the derivatives of acetic acid, we easily observe the depressing effect of the unsaturated nucleus, the diphenylacetic acid being a slight exception ; but when we compare the corresponding esters of carboxime the diphenylacetic acid is no longer exceptional. The very low rotatory power of the menthyl

* Rupe and Busolt, *Ann.*, **369**, 368 (1909).

† *Ibid.*, *Ann.*, **369**, 356 (1909).

‡ Rupe and Jäger, *Ann.*, **402**, 149 (1913).

§ Rupe and Iselin, not yet published.

|| McKenzie and Martin, *Trans. Chem. Soc.*, **103**, 112 (1913).

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ester of triphenylacetic acid was found at the same time by Tschugaeff* and by my student Ahner.† Tschugaeff pointed out in his paper that this substance, which has an irregular rotatory dispersion, possesses an absorption

TABLE XI.

	$[\alpha]_D$.
$C_6H_5 \cdot CH \cdot (OH)CH_2 \cdot C(C_6H_5)_2 \cdot OH \dots \dots \dots$	43·7
$C_6H_5 \cdot CH(OH) \cdot CH_2 \cdot C(CH_3)_2 \cdot OH \dots \dots \dots$	72·3
$C_6H_5 \cdot CH_2 \cdot CH(OH) \cdot C(C_6H_5)_2 \cdot OH \dots \dots \dots$	138·0
$C_6H_5 \cdot CH_2 \cdot CH(OH) \cdot C(CH_3)_2 \cdot OH \dots \dots \dots$	67·6

band in the ultra-violet, which he regards as the source of the anomalous rotatory dispersion. That may be so, but it is only one example. In the last two years with my students I have measured the rotatory dispersions of

TABLE XII.

	$[\alpha]_D$.	M_D .
$C_6H_5 \cdot CH_2 \cdot CO \cdot OH \dots \dots \dots$	67·57	185·1
$C_6H_5 \cdot (C_6H_5)_2CH \cdot CO \cdot OH \dots \dots \dots$	66·70	226·8
$C_6H_5 \cdot (C_6H_5)_3C \cdot CO \cdot OH \dots \dots \dots$	3·44	—

optically-active compounds with accumulations of unsaturated groups, and comparatively low rotations, but we have never found an anomalous one.

When we compare the menthyl esters of benzoic, *p*-methylbenzoic and *p*-phenylbenzoic acids, we find that the methylated derivative has the greatest and the phenyl derivative the lowest rotatory power (95·2° and 80·7°).

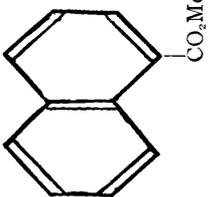
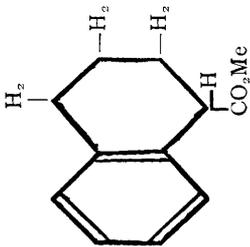
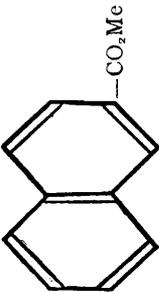
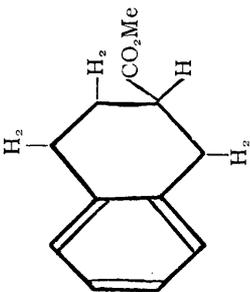
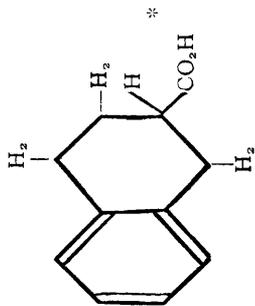
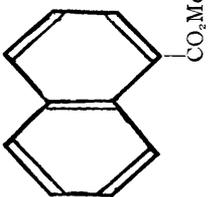
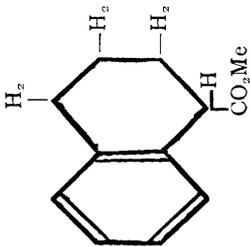
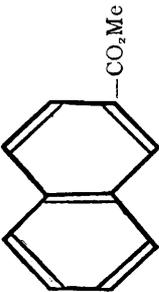
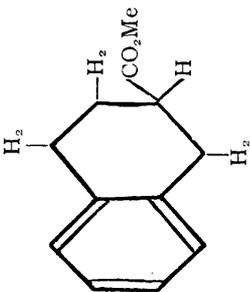
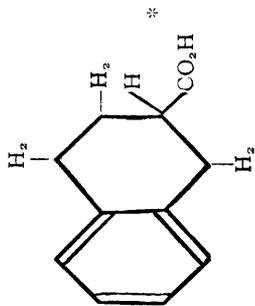
Influence of the Naphthalene Group.

May I be allowed to refer briefly to the influence of the naphthalene group? On comparing the optical rotations of the menthyl esters of the two naphthylcarboxylic acids,‡ we observe in the α acid the influence of the neighbourhood of the second nucleus, but the difference between these acids and benzoic acid is, on the whole, of no great importance. We know from Bamberger's classical work that naphthalene is quite a different thing from benzene, but when we reduce one of its nuclei, the other, which does not carry the carboxyl-group, becomes a true benzenoid nucleus. We may therefore consider the hydro-aromatic acids as phenyl derivatives of cyclohexane-

* Tschugaeff, *Ber.*, **35**, 2759 (1912).

† Not yet published.

‡ Rupe and Silberberg, *Ann.*, **327**, 168 (1903); Rupe and Münter, *Ann.*, **373**, 121 (1910).

$[\alpha]_D$	M_D	$[\alpha]_D$	M_D	$[\alpha]_D$	M_D
79°08	—	91°30	—	—	1020 Phenyl 986 <i>α</i> -Naphthyl
					$C_{10}H_{14}O : CH \cdot C_6H_5 \dots$ $C_{10}H_{14}O : CH \cdot C_{10}H_7 \dots$
47°57	—	53°04	—	—	...
—	92°1	—	87°1	—	...
					...

* The two optically active tetrahydronaphthoic acids have been prepared by Pickard and Yates, *Trans. Chem. Soc.*, **89**, 1104. Here the *α*-acid possesses in benzene solution the greater rotation.

carboxylic acids or as analogues of phenylacetic acid. In conjunction with Iselin* I was successful in preparing a series of derivatives of methylene camphor—for instance naphthylmethylene camphor. Its specific rotation is considerably less than that of phenyl methylene camphor (the benzylidene camphor of Haller); the molecular rotation is almost the same.

Theories as to the Influence of Unsaturation.

Until to-day we have had no satisfying explanation of the increasing effect of an unsaturated group, and still less of its opposite influences. The phenyl group and the double bond contain more energy than the saturated groups. Perhaps we shall be able to find here the germ of a theory; but in a recent paper Auwers, Eisenlohr and Roth † have shown that a conjugated double linking contains less energy than a non-conjugated, *i.e.*, that the former, in contradiction to its optical behaviour, is really the more saturated. So also the triple bond, in spite of its great energy-content, has generally a smaller influence on the rotatory power than the ethenoid bond. We must therefore look elsewhere for an explanation.

The molecular volume of unsaturated compounds is generally greater than that of saturated ones. This suggests the hypothesis that the influence of optically active groups is such that the four groups or radicals, which surround the asymmetric carbon atom, suffer a certain pressure or deformation from the larger volume.

That perhaps may give an explanation of the influence of an unsaturated complex near to the asymmetric carbon, but not of the strong effect of a remote unsaturated group, especially when there is an accumulation, unless we adopt the hypothesis of the lever mentioned by me just now.

When we try to deal with the theories of the supplementary valencies, perhaps in the light of Stark's hypothesis of the valency-electrons, we encounter the same difficulty; it gives an explanation for the reaction near the asymmetric carbon, but only of that.

In conclusion, I wish to discuss briefly the following question: Are we already able to make use of optical rotation as a help in determining the constitution of optically-active organic compounds? The refraction in many cases is of great value for this purpose. The optical rotation cannot yet be employed to the same extent, but I am of opinion that, in the hands of a chemist with some knowledge of this subject, this method may frequently be of real service.

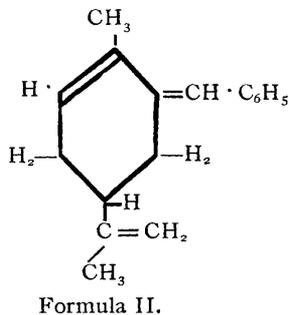
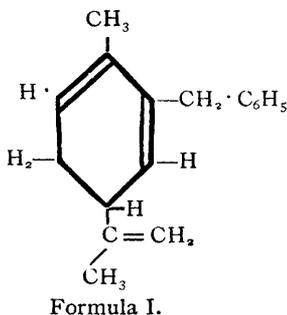
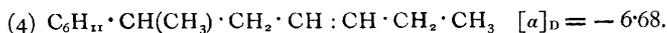
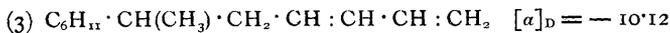
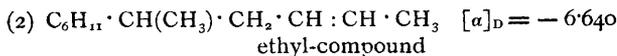
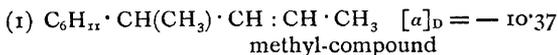
May I be allowed to give here some examples borrowed from the work of others, as well as from my own? When I found, with Jäger, ‡ that the product of the reaction of methyl magnesium bromide with citronellal gave a much larger rotation than the other alkyl-derivatives, for instance, the ethyl-compound, we could only suppose that in this methyl-compound (1) the double bond was nearer to the asymmetric carbon atom than in the other homologues, *i.e.*, the ethyl compound (2); this supposition was confirmed by oxidation with ozone. When, in the course of the same work, the allyl-derivative (3) showed a greater rotatory power than the corresponding propyl-compound (4), we were able to consider with much probability

* Rupe and Iselin, not yet published.

† *Ber.*, **43**, 1063 (1910); *Ann.*, **373**, 239 (1910).

‡ Rupe and Jäger, *Ann.*, **402**, 149 (1913).

that the increased rotation was due to a conjugation, and this was confirmed by measurements of refraction.



On treating carvone with benzyl magnesium chloride* two isomeric hydrocarbons were obtained, the first with a great, the second with a rather low optical rotation. There is no doubt that the former has the Formula I, the latter the Formula II. The yield of these compounds being poor, we have not yet been able to determine the constitution in a chemical way. The refraction for both is nearly the same, and I do not think that oxidation would serve to differentiate the two compounds.

Every one who has worked in this field knows that the rotatory power is much more sensitive to changes of constitution than the refraction. One may recall how the transition of the enolic to the ketonic form of Forster's † benzoylcamphor is marked by the changing of the rotation, and we observe the same phenomena when the menthyl ester of phenylacetoacetic acid changes its rotation rapidly under the influence of piperidine. ‡

One could easily multiply examples. There is, for instance, no doubt that when we have two isomeric unsaturated acids, both optically active, the one with the greater rotation possesses the double linking nearer to the asymmetric carbon. Trouble generally comes when phenyl groups enter the chain, and it is one of the problems of our science to find out the very complicated and irregular behaviour produced by the accumulation of unsaturated groups. The solution of this problem: tis a consummation devoutly to be wished!

* Rupe and Tomi, not yet published.

† Forster, *Trans. Chem. Soc.*, **79**, 994.

‡ Rupe and Lenzinger, *Ann.*, **395**, 91 (1912); **398**, 372 (1913).