The less soluble salt yielded *d*-ascaridolic acid. 2.0545 g. made up to 25 cc. solution in chloroform at 24° in 200 mm. tube = 2.29° to the right. $[\alpha]_D = +13.93°$, melting point 129–130°.

The more readily soluble salt yielded the *l*-ascaridolic acid, which also melts at 129–130°.

2.0431 g. made up to 25 cc. solution in chloroform at 24° in 200 mm. tube = 2.25° to the left.

$[\alpha]_D = -13.77°$.

WASHINGTON, D. C.

OPTICAL ROTATORY POWER AND CHEMICAL CONSTITUTION.

By L. G. Wesson.

Received October 19, 1914.

Pickard and Kenyon, in a series of valuable investigations on the "Dependence of Rotatory Power on Chemical Constitution,"[1] have determined the molecular rotatory power of over 100 closely related compounds. The list includes methyl ethyl carbinol and its homologs up to the ethyl tridecyl member, isopropyl methyl carbinol and its homologs up to the isopropyl decyl member, and the esters of the methyl carbinol series with the homologous *n*-aliphatic acids from acetic up to dodecoic, myristic, palmitic and stearic acids.

From these experimental results, which are to be made the basis of the present paper, Pickard and Kenyon derive an hypothesis[2] which is "based merely on a consideration of the space occupied by the four groups attached to the asymmetric carbon atom" and "appears to explain the results obtained for the three series of carbinols, as well as those obtained for eight series of simple esters derived from the 'methyl' series of carbinols."

"In a homologous series of optically active compounds represented by *Cabcd*, the usual effect of increasing the size of *d* (representing the growing chain) is to alter in a regular manner (usually to increase) the molecular rotary power of the compounds."

"When the groups (or atoms) represented by *a*, *b*, and *c* occupy a relatively small space, as, for example, in the 'methyl' series of carbinols, $CH_3.CH(OH).R$, the values of the molecular rotary powers of the homogeneous compounds increase regularly with the increasing size of the chain, and only in solution are affected by the peculiar configuration of the chain, when this returns upon itself."

"When, however, the space occupied by the groups (or atoms) *a*, *b*

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[1] Part I, *J. Chem. Soc.*, **99**, 45 (1911); Part II, *Ibid.*, **101**, 620 (1912); Part III, *Ibid.*, **101**, 1427 (1912); Part IV, *Ibid.*, **103**, 1923 (1913); Part V, *Ibid.*, **105**, 830 (1914); also, *Ber.*, **45**, 1892 (1912); *Chem. News*, **108**, 163 (1913); and *Trans. Faraday Soc.*, **1914** (*C. A.*, **8**, 2339).

[2] Part IV, *J. Chem. Soc.*, 103, 1930 (1913).

and *c* is larger, the increase in molecular rotatory power may become less regular as *d* increases in size; either (1) it may be specially affected, when the chain returns on itself, as in the 'ethyl' series, $C_2H_5.CH(OH).R$, or (2) there may be a relatively large increase until *d* contains five carbon atoms with an increase of a much smaller order beyond; as, for example, in a series of esters, such as those of secondary octyl alcohol with normal aliphatic acids, in which there is a large increase in the value of the molecular rotatory power for each member of the series up to the normal valerate, and a still further, but relatively much smaller, increase for each member from the valerate to the palmitate; or (3) when the space occupied by the groups *a*, *b* and *c* is still greater, an 'approximate maximum' is reached when the growing chain contains fewer than five carbon atoms; as, for example, for the carbinols of the isopropyl series, $CH(CH_3)_2.CH(OH).R$ (when these are examined in the homogeneous state), and in a series of *n*-dodecoates of the 'methyl' carbinols, $R.CH(OCO.C_{11}H_{23}).CH_3$, in both of which the values of the molecular rotatory power increases rapidly up to that for the member with *R* containing four carbon atoms with a much smaller increment for the higher members."

In brief, the differences between the curves for the various series are ascribed by Pickard and Kenyon to the differences in the amount of space occupied by the atoms or groups other than the growing chain, as well as that occupied by the growing chain itself.

P. F. Frankland, to whom so much is due in the field of optical activity, expressed an opinion very similar to the above in 1912.[1]

"It might at first sight be supposed," says Frankland, "that if such steric interference (in compounds with a chain of 5 carbon atoms attached to the asymmetric one[2]) were the cause of this limitation (in the increase or decrease of the molecular rotatory power), the maximum or constant molecular rotation should always occur at the same term in all homologous series. This, however, is not found to be the case, and it would appear probable that the term at which such interference occurs will depend, not only on the length of what may be called the homologous chain itself, but also on the other groups, which are present in the molecule, and which may themselves interfere with the normal development of the homologous chain. * * * * More recently, Pickard and Kenyon have prepared a similar homologous series from isopropyl carbinol, and in this it might be anticipated that the isopropyl group should give rise to more interference than the methyl group in the previous series."

The writer believes that these phenomena, explained by Pickard and

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[1] Presidential address, *J. Chem. Soc.*, 101, 654 (1912).

[2] Frankland early recognized the special influence of carbon chains with 5 (or 6) and 9 (or 10) carbon atoms in phenomena of optical activity. See *J. Chem. Soc.*, 75, 368 (1899).

Kenyon and by Frankland on the basis of the space occupied by the groups attached to the asymmetric atom and their interfering influence upon each other, should rather be ascribed to another factor, namely, the attractive forces exerted by the groups upon the asymmetric atom.[1]

If these tables and curves, compiled from Pickard and Kenyon's experimental work, be examined, the following significant facts will be observed:

1. The molecular rotation of the series of ethyl carbinols (Table I and Fig. 1) has a smaller value throughout than has that of the methyl series, while both the methyl and ethyl series have smaller values than the isopropyl series.

TABLE I.—MOLECULAR ROTATORY POWERS OF THE NORMAL SECONDARY ALCOHOLS.[2]

	In the homogeneous state.			Dissolved in ethyl alcohol.[6]		
$[M]^{20}_{D}$.	Methyl.[3]	Ethyl.[4]	Isopropyl.[5]	Methyl.	Ethyl.	Isopropyl.
Methyl	0°	10.30°	4.3°	0°	10.77°	4.70°
Ethyl	10.3	0	15.4	10.77	0	16.73
n-Propyl	12.1	2.01	24.7	13.60	1.17	27.07
n-Butyl	11.8	9.43	33.3	12.95	11.17	35.97
n-Amyl	12.0	10.69	32.9	13.28	14.47	38.24
n-Hexyl	12.7	10.63	33.9	12.73	13.86	38.36
n-Heptyl	12.9	10.58	..	13.10	9.81	...
n-Octyl	13.7	10.74	34.5	14.04	10.69	39.99
n-Nonyl	14.0	11.09	..	13.95	11.35	...
n-Decyl	14.5	12.44	34.5	14.76	13.46	39.38
n-Undecyl	14.4	12.56	..	14.74	13.38	...
n-Dodecyl	..	12.61	..	...	12.44	...
n-Tridecyl	..	12.38	..	...	12.75	...
n-Pentadecyl	..	12.88	..	...	12.99	...

[1] The attention of the writer has been recently called to a significant sentence by Michael, *Ber.*, **34**, 3647 (1901); *J. prakt. Chem.*, [2] **75**, 117 (1907), in which he states that carbon asymmetry is to be considered the result of the chemical-mechanical influence or tension of four unequal forces on an atom, rather than a purely chemical effect.

Doubtless the idea that optical activity may be due to differences of forces of attraction for the asymmetric atom has also occurred to others.

A little different are the theories of Baly and Winther.

Baly, *Z. Electrochem.*, **17**, 211 (1911), believes that optical activity is due to the asymmetric field caused by the merging of the lines of force from the residual affinities of the groups about the asymmetric atom.

Winther, *Z. physik. Chem.*, **60**, 590, 641, 756 (1907), claims that every change in the optical rotation of a substance is connected as effect to cause with a volume change, and every volume change, due entirely and solely to a pressure change (internal or external) is accompanied by a proportional change in the optical rotation.

[2] In Figs. 1 and 2 which represent the table, the curves have been drawn to show only the variations common to both the homogeneous and dissolved states.

[3] Pickard and Kenyon, *J. Chem. Soc.*, **99**, 49 (1911).

[4] *Ibid.*, **103**, 1925 (1913).

[5] *Ibid.*, **101**, 624 (1912).

[6] *Ibid.*, **103**, 1957–8 (1913).

TABLE II.—MOLECULAR ROTATORY POWERS OF THE ESTERS OF THE METHYL CARBINOLS.[1]

	$[M]_D^{20}$ of the ester of					
	Me. ethyl carbinol.	Me. propyl carbinol.	Me. butyl carbinol.	Me. amyl carbinol.	Me. hexyl carbinol.	Me. nonyl carbinol.
Acetate	29.70°	22.30°	14.59°	13.00°	11.77°	11.28°
Propionate	31.00	23.66	15.43	14.40	12.99	11.75
Butyrate	31.63	24.92	18.62	18.91	17.90	17.68
Valerate	32.74	27.54	20.75	20.52	19.60	19.09
Hexoate	32.10	...	21.68	21.34	20.42	19.91
Heptoate	32.31	...	22.17	21.72	20.78	20.37
Octoate	32.28	...	...	21.95	21.12	...
Nonoate	32.17	...	22.69	22.26	21.50	21.25
Undecoate	32.48	...	22.55	22.59	21.91	21.43
Dodecoate	32.48	28.19	22.68	22.58	21.84	21.91
Myristate	32.21	...	23.10	22.52	22.40	21.87
Palmitate	31.99	...	...	23.10	22.57	...
Stearate	31.92	...	...	23.15	22.61	...

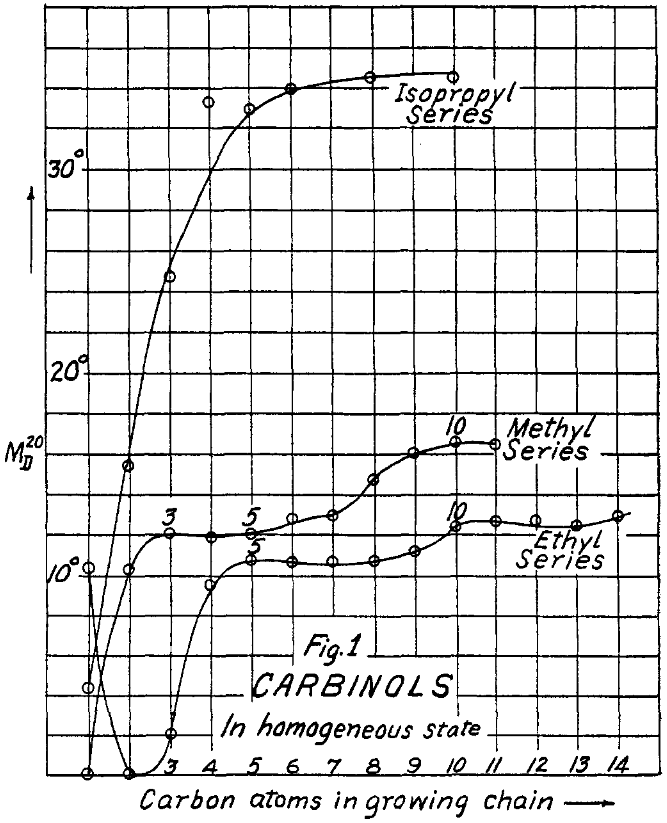

Fig. 1
CARBINOLS
In homogeneous state

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[1] Pickard and Kenyon, *J. Chem. Soc.*, 105, 831 (1914).

2. In the *ethyl* series of carbinols there are found exaltations in the curve at the points at which the growing chain contains 5 or 10 carbon atoms, and is therefore of the most favorable length to return upon itself toward the asymmetric atom. This exaltation for the ethyl carbinols is much more pronounced when the rotatory power is measured upon the solution of the carbinols (Fig. 2), and solution has been found in general to bring out and magnify such effects.[1]

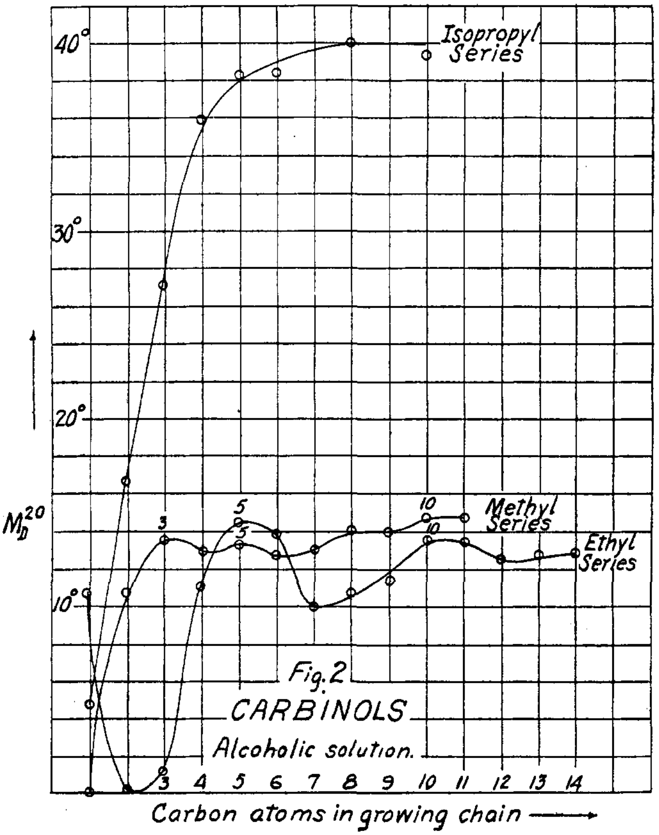

Fig. 2
CARBINOLS
Alcoholic solution.

In the *methyl* series such an exaltation cannot be detected at the points 5 and 9, or 10, until the carbinols are dissolved, while in the *isopropyl* series even solution is not sufficient to bring out a corresponding exaltation.

3. In the curves of the esters (Table II and Fig. 3), if the acid is kept constant in each curve and the alkyl radical gradually increases, an exaltation is found when the alkyl group contains 5 carbon atoms.

In the corresponding curves in which the alkyl radical is kept constant

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[1] Frankland, *J. Chem. Soc.*, 101, 660 (1912); Pickard and Kenyon, *Ibid.*, 103, 1928 (1913).

in each curve and the length of the acid chain gradually increases (Table II and Fig 4), an exaltation is found when the acid contains 4 and 5 carbon atoms.

4. In all of these series of curves, the exaltations become, in general, less marked as the value of the molecular rotatory power increases

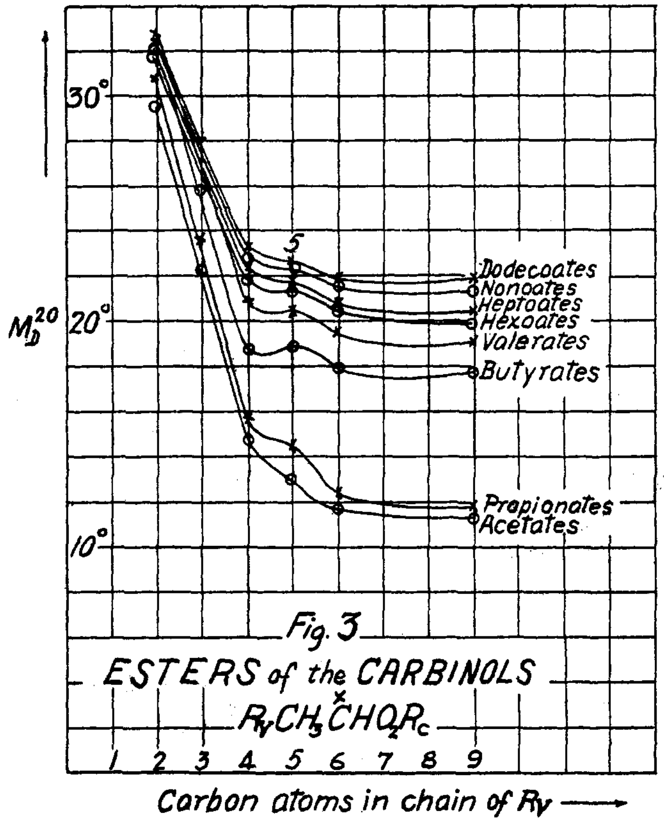

Fig. 3.

ESTERS of the CARBINOLS $R_yCH_3\overset{*}{C}HOHR_c$

According to the hypothesis supported in this paper these regularities are to be accounted for by the following considerations:

1. The alkyl radicals in general, as is shown by their chemical behavior (*e. g.*, dissociation constants of the aliphatic acids) in a number of various types of compounds, experience a much sharper transition in properties as one passes from the methyl to ethyl than from the ethyl to propyl group, likewise a greater transition occurs from ethyl to propyl than from propyl to butyl, and so on.

One of the properties, which thus changes, is the positivity of the alkyl radical[1] toward such a group as for example—CRHOH of the optically

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[1] Michael, *J. prakt. Chem.*, [2] 60, 286 and 409 (1899); *Über einige Gesetze und deren Anwendung in der organischen Chemie.* See especially p. 432 in this connection.

active compounds which we are considering. The methyl group will exert upon the central carbon atom of this group an attractive force which will differ more from that of an ethyl group than would an ethyl and isopropyl group when compared in the same way. Propyl and butyl likewise differ, but to a less extent than do ethyl and propyl. As the alkyl radical increases in length, the differences between the relative positivity of the successive homologs decreases. Similarly, between a normal alkyl radical such as propyl and a branched one as isopropyl, a still greater difference of attractive force would be expected.[1]

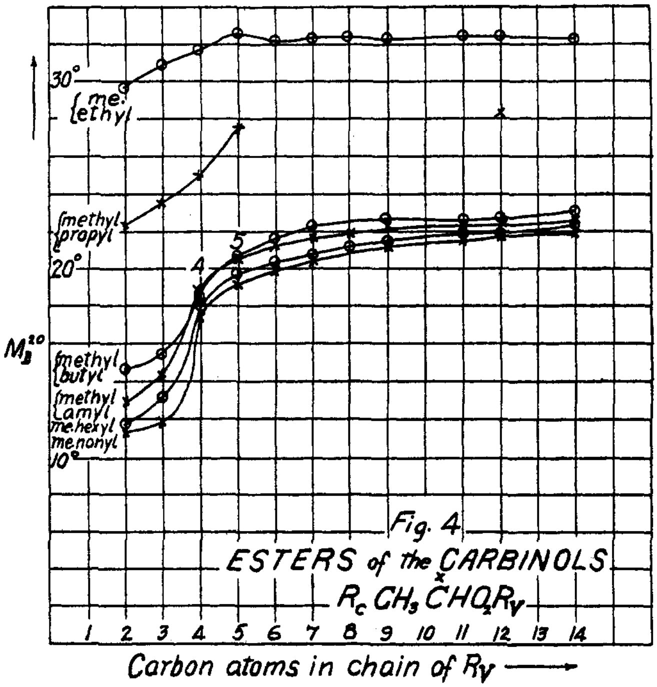

Fig. 4

ESTERS of the CARBINOLS

$R_c CH_3 \overset{x}{C}HO_2 R_V$

We have then in the ethyl series from ethyl propyl carbinol on, two alkyl groups united to the asymmetric atom, which differ less in the respective forces with which they attract that atom than do the corresponding groups in the methyl carbinol series. The optical rotatory power of the ethyl carbinol series is, therefore, smaller than that of the methyl series.

In the isopropyl series this difference is still greater than in the methyl carbinols (*e. g.*, isopropyl and ethyl, isopropyl and propyl, etc.), and we find that the rotatory power is correspondingly much larger than in the two preceding series.

2. In discussing the attractive forces, the attraction of a group as a whole should be considered rather than that represented by the particular

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[1] Michael, *Loc. cit.*, p. 432.

atom which happens to be adjacent to the asymmetric one. Thus all of the atoms perform their share to a degree which depends upon their position in the molecule.[1] This effect may be exerted through other atoms or through space, the combined influence in alkyl radicals decreasing in the order 2–3–5–6–4–7–(9–10–11)–8.

The atoms 5 and 6 owe their unexpectedly great influence to the fact that they occupy a position in which they are able to approach comparatively near atom 1 as the growing chain in its natural configuration returns upon itself. This sudden increase of attractive force is necessarily small in comparison with the total force exerted by the group for the asymmetric atom, yet if two of the groups are nearly equal this change may be quite appreciable in comparison with the already existing difference, and, as in the ethyl series, quite an appreciable exaltation in the rotatory power may be observed at this point.

In the methyl series, where the difference between the attractive forces of the two alkyl groups is greater, the sudden increase due to the close approach of atom 5 to the asymmetric atom is much smaller in comparison with the already existing difference. The effect of this secondary influence on the optical activity is therefore so small that it is observable only when the carbinols are in a dissolved condition.

The difference between the alkyl groups is already so great in the isopropyl series that no appreciable effect is produced on their relative values by the return of the alkyl chain upon itself, and, as would be expected, no exaltation can be observed at this point in the case of the isopropyl series, even if the measurements are made upon the dissolved substance.

3. Similar considerations are applicable in the case of the esters of the carbinol. The return of the chain upon itself produces an additional attraction of the whole group for the asymmetric atom, and, therefore, a point of inflection in the rate of change of the optical activity.

If, as in Fig. 3, the normal alkyl group united to the asymmetric atom is gradually increased in size, an exaltation is found at the point corresponding to a chain of five carbon atoms, whereas, if the acyl group is similarly lengthened, an exaltation is found when the total chain united to the asymmetric atom consists of one oxygen and four or five carbon atoms.

4. If optical activity is dependent, as claimed, upon differences in the attractive forces exerted by the atoms or groups for the asymmetric atom, the smaller the difference between two of the groups, other differences being constant or practically so, the smaller will be the optical

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[1] Michael, *Loc. cit.*, pp. 331 and 335. THIS JOURNAL, **34**, 849 (1912). The literature contains many investigations which demonstrate the marked influence of the position of substituents on optical activity. See, *e. g.*, Rupe, *Ann.*, **369**, 311 (1909).

rotatory power. Thus, the smaller the rotatory power, the greater would be the expected effect upon this by a given small change in the difference between the attractive forces of these two almost equal groups. The observed facts indicate it to be a general rule that as the molecular rotatory power decreases in a group of curves the exaltations or other uniform deviations become increasingly large.

Product of Asymmetry.

The data at hand are not sufficient to indicate whether or not the molecular rotatory power is a function of the product obtained by multiplying together the differences between the attractive forces exerted by the four atoms or groups upon the asymmetric atom; that is,

$$F\ (A-B)\ (A-C)\ (A-D)\ (B-C)\ (B-D)\ (C-D)$$

As each atom or group affects the character (positivity) of the asymmetric atom, it is likely that a given atom or group would possess no constant value in this relation even when very similar compounds are compared. It is therefore not at all surprising that repeated attempts to derive constants for the various radicals and atoms have not met with success.[1]

Effect of Mass on Optical Activity.

That the mass of an atom or a group united to the asymmetric atom may be of some significance in determining its effect upon the optical activity of the molecule is not excluded by the theory of attractive forces. At the best, however, the effect of mass seems to be only auxiliary to the larger one of relative attractions. Examples of this are familiar in the literature of optical activity.

A possible mode may be suggested here by which the asymmetry of the attractive forces exerted upon an asymmetric atom may be conceived to be connected with its effect upon the plane of polarization of light.

If, in a symmetrical molecule of the type *Ma a b c* a, plane were passed through atoms *M*, *b* and *c*, the atoms *a* and *a* would be symmetrically situated with respect to the plane *Mb c*. The atoms in a molecule, in their oscillations toward and away from each other must move in paths which express the resultant of all the forces which are exerted upon them. Therefore, in a molecule of the type *M a a b c*, one can be certain that the path described by *M* will either lie in the plane *Mbc*, or, if it does not do this, it will, as *a* and *a* are alike, lie on the average or the same extent

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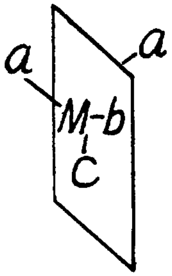
[1] Compare this product with *a*, the product based on asymmetry of mass; Crum Brown, *Proc. Roc. Soc. Edinb.*, 17, 181 (1890); Ph. Guye, *Compt. rend.*, 110, 714 (1890); *b*, the product based on empirical constants for various atoms and radicals; Bose and Willers, *Z. physik. Chem.*, 65, 695 and 702 (1909); Walker, *J. Phys. Chem.*, 13, 574 (1909).

on one side of this plane in one half of the total number of molecules as it does on the other side of the other half.

In an asymmetric molecule, however, represented by *M abcd*, the path of *M* would not be expected to average the same in one direction in one-half of the total number of molecules as it does in the other direction in the other half, unless an equal number of the stereo-chemically opposite molecules *M bacd* be present with the molecules *Mabcd.*



To the mean asymmetric path taken by the asymmetric atom (carrying an electric or magnetic field)[1] is ascribed the optical rotatory power of the asymmetric molecule. Any influence which increases the effective asymmetry of this orbit will, according to this hypothesis, increase the observed molecular rotatory power of the substance.

A theory which attempts to point out the cause of the phenomenon of optical activity must fulfill at least this important condition—it must account for an asymmetry such that polarized light passing through the molecules of an active substance in one direction is affected to a greater degree than in the other. The postulate just described of the asymmetrically moving atom answers this requirement in the following way:

Let the motion of the asymmetric atom be simplified at any given instant, and during the time required for the passage of a light wave through the space under its influence, to the form of a portion of a helix, the whole helix, of which this is a portion, representing not the actual path of the atom, but rather a basis on which the portion may be considered in comparison with the asymmetric atoms of the other molecules.[2]

Consider an active substance which has been completely resolved into its optically opposite components, and which, therefore, contains only those molecules possessing one of the two possible optical configurations. At any instant, the asymmetric atom, *M*, is moving in one-half the total number of molecules in one general direction, *e. g.*, toward atom *d*, with a motion whose resultant toward *d* will require a mean of *s* turns and time *t* for completion. In the other half, the motion of *M* in the same instant is *away* from atom *d*, and is represented by turns s' and time t'. Of the first, one-half .of the molecules will face in one general direction and the general direction of the propagation of the light will coincide with that

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[1] See especially, in this connection, P. de Heen, *Bull. Acad. roy. Belgique,* Classe des Sciences, 1913, p. 680; *Chem. Zentr.*, 1914, I, 599.

[2] The whole motion of the asymmetric atom may, perhaps, according to this conception, be described as following a curved orbit with a simultaneous forward motion, the axis of the orbit at the same time turning eventually toward every conceivable direction. The familiar wound ball of twine furnishes a homely illustration of this path. The harmonic motions finally run their course, the atom arrives again at its starting point, and is ready to repeat its complex revolution.

of the motion of M. In the other half of this group, the light and atom will be moving in opposite directions, and, as the light must occupy a finite time in its passage through the field of influence of M, the effect of M on the light will be greater in those molecules in which the two directions coincide than can be compensated for by the equal number of molecules facing in the opposite direction in which the light and the atom approach each other and pass, but do not move together. Thus, for the molecules in which M is in motion *toward* d, there will be a resultant uncompensated effect upon the light.

The same holds true in a similar way for the molecules in which M is in motion *away* from d, but the effect which is caused by an atomic motion represented by s' turns and time t' will be different in amount from that caused by the first group. Thus a net rotation will be observed upon the emergent light.[1]

Conclusion.

The hypothesis here presented was worked out by the author in 1912. At that time no mention could be found that such an hypothesis had ever been suggested to account for the phenomena of optical activity, or, in fact, since, has one been found in the literature devoted to optical activity. The recent experimental results of Pickard and Kenyon, forming as they do, such a complete series of comparable data, have been used in the preceding paper to the exclusion of other and less conclusive results upon which previous deductions had rested. These offer for the first time an indication of the validity of the hypothesis that the phenomena of optical activity depend primarily upon an asymmetry of the attractive *Forces* exerted upon an asymmetric atom by its four adjacent atoms or groups.

CAMBRIDGE, MASS.

[CONTRIBUTION FROM THE KENTUCKY AGRICULTURAL EXPERIMENT STATION.]

THE OCCURRENCE AND SIGNIFICANCE OF MANGANESE IN THE SEED COAT OF VARIOUS SEEDS.

BY J. S. MCHARGUE.

Received October 8, 1914.

It has been observed by investigators that the different organs of some plants show considerable variation in the amount of manganese they contain. According to the researches of Jadin and Astruc,[2] the

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[1] The possibility of the existence of optically active individual *symmetrical* molecules is suggested by the above, according to which a symmetrical and an unsymmetrical molecule may differ only in that the former produces an effect on the light which is compensated for by other molecules while the latter produces an uncompensated effect.

[2] Jadin and Astruc, *Compt. rend.*, 156, 2023 (1913).