corresponding hydrocarbon. The yield was 4 g. of a product, b. p. 74–76° (3 mm.); n^{20}_D 1.5074; d^{20}_4 0.9513.

Anal. Calcd. for $C_{13}H_{20}$: C, 88.55; H, 11.45. Found: C, 88.46; H, 11.45.

Perhydrophenanthrene.—A solution of 4.5 g. of Δ^{11}-dodecahydrophenanthrene in 60 cc. of methylcyclohexane was reduced with hydrogen over Raney nickel catalyst at 250° and 1500–2000 lb. pressure for eight hours. From this reaction mixture, 2 g. of perhydrophenanthrene purified by boiling with metallic sodium was obtained. It boiled at 86–89° (2 mm.); n^{20}_D 1.5011; d^{20}_4 0.9447.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.41; H, 12.59. Found: C, 87.38; H, 12.56.

In a similar manner, 10 g. of phenanthrene was reduced.[19] In order to obtain complete reduction, it was necessary to isolate the product from the reduction mixture and reduce a second and third time with fresh catalyst each time. Two products were obtained on fractionation of the reduced hydrocarbon. These appeared to be identical with perhydrophenanthrene reported previously.[9] The first fraction (about 1 g.) boiled at 90–93° (2.5 mm.); n^{20}_D 1.4994; d^{20}_4 0.9385.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.41; H, 12.59. Found: C, 87.30; H, 12.66.

The second fraction (2 g.) boiled at 93–96° (2.5 mm.); n^{20}_D 1.5019; d^{20}_4 0.9437.

Anal. Calcd. for $C_{14}H_{24}$: C, 87.41; H, 12.59. Found: C, 87.53; H, 12.46.

Attempts were made to dehydrogenate the perhydrophenanthrene obtained from our synthetic experiments, and also that obtained by the direct hydrogenation of phenanthrene by heating samples with selenium at 300–320° for twenty-five hours. These attempts were unsuccessful.

Decahydro-1,2-cyclopentanonaphthalene.—The octahydro-1,2-cyclopentanonaphthalene was reduced with hydrogen and Raney nickel catalyst in the same manner as described for the other hydrocarbons. From 1.5 g. of the unsaturated compound, about 0.5 g. of a colorless liquid boiling at 71–72° (2.5 mm.) was obtained: n^{20}_D 1.4895; d^{20}_4 0.9241.

Anal. Calcd. for $C_{13}H_{22}$: C, 87.55; H, 12.45. Found: C, 87.40; H, 12.66.

Summary

The reaction for converting dieneynes to cyclohexenone derivatives has been extended to produce derivatives of dodecahydrophenanthrene and octahydro-1,2-cyclopentanonaphthalene.

URBANA, ILLINOIS RECEIVED APRIL 23, 1936

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[19] We are indebted to Professor Homer Adkins for his aid with this experiment.

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

Suggestion for an Empirical Method for Predicting the Configuration of Optically Active Carbon Compounds

BY RUSSELL E. MARKER

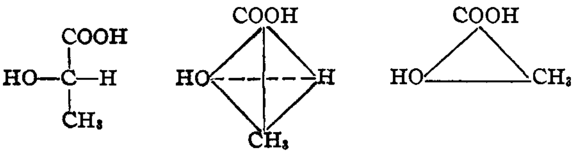
A knowledge of configurational relationships is necessary in any study of the Walden inversion.

As has been shown by Levene and his co-workers[1] all rules for determining these relationships have only limited application. Only the most difficult and painstaking experimental methods have given these relationships.

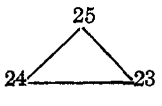
After many attempts at arranging the mass of available data, the table given was constructed largely from measurements by Levene and his co-workers, and to a lesser extent from those by Pickard and Kenyon[2] and their collaborators. The lower portion of the table contains the six more highly polar groups arranged in order of *increasing* levorotation instead of the *decreasing* order used in the upper part of the table. It should be noted carefully that this table and its applications are based only on the rotations of pure liquids at about 25° for the sodium D line.

From the first four columns in the table is obtained the *numerical order* of the groups listed in the R column. Sufficient data are not now available to place conclusively other groups in this series.

Since lactic acid is the standard reference substance for the determination of configurations, the application to it of the ordinal numbers in the last column is appropriate.



Levorotatory lactic acid



The two triangles represent the face of the tetrahedron if the H corner is placed to the back. The

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[1] Levene and co-workers, *J. Biol. Chem.*, 1925 to date.

[2] Pickard and Kenyon, *J. Chem. Soc.*, 1912 to date.

TABLE I

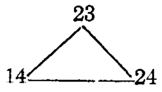
MAXIMUM MOLECULAR ROTATIONS WITHOUT SOLVENT OF CONFIGURATIONALLY RELATED COMPOUNDS

$C_5H_{11}—\overset{H}{\underset{R}{C}}—CH_3$	$C_4H_9—\overset{H}{\underset{R}{C}}—CH_3$	$C_3H_7—\overset{H}{\underset{R}{C}}—CH_3$	$C_2H_5—\overset{H}{\underset{R}{C}}—CH_3$	R	Ordinal numbers
−14.7	−16.8	−21.3	−38.8	$—CH_2CH_2Br$	1
−9.3	−11.9	−14.9	−21.3	$—C_4H_9$-*i*	2
−6.2	−8.3	−14.5	−21.9	$—CH_2CH_2CH_2Br$	3
−4.0	−5.3	−7.8	−14.9	$—CH_2CH_2CH_2CH_2Br$	4
−1.9	−4.1	−6.9	−13.6	$—CH_2CH_2COOH$	5
−1.7	−2.8	−5.9	−13.0	$—CH_2CH_2CH_2COOC_2H_5$	6
−0.5	−2.3	−5.5	−12.7	$—CH_2CH_2COOC_2H_5$	7
− .8	−1.7	−3.7	−11.1	$—CH_2CH_2CH_2COOH$	8
− .2	−1.5	−3.5	−11.9	$—C_5H_{11}$-*i*	9
.0	−0.8	−2.4	−12.5	$—C_5H_{11}$	10
+ .8	.0	−1.7	−11.4	$—C_4H_9$	11
+1.9	.0	−1.7	−12.0	$—CH_2CH_2CH_2CH_2OH$	12
+2.6	+0.7	0.0	−11.9	$—CH_2CH_2CH_2OH$	13
+2.4	+1.5	.0	−10.0	$—C_3H_7$	14
+3.6	+1.9	+ .4	−10.6	$—CH_2CH_2NH_2$	15
+4.2	+2.9	+ .7	−11.4	$—CH_2COOC_2H_5$	16
			− 9.2	$—CH_2C_6H_5$	17
+6.1	+4.0	+2.1	− 9.0	$—CH_2CH_2OH$	18
+8.1	+6.1	+3.6	−10.3	$—CH_2COOH$	19
+12.5	+11.4	+10.0	0.0	$—C_2H_5$	20
Increasing dextro			+ 5.2	$—CH_2OH$	21
Increasing dextro			+28.3	—*i*-Propyl	22
				—Methyl	23
−12.5	−12.2	−12.1	−10.3	—OH	24
−25.0	−24.3	−21.4	−18.0	—COOH	25
Levo	−30.7	−27.5	−22.9	$—COOC_2H_5$	26
Levo	−39.0	−38.0	−36.6	$—C_6H_5$	27
−50.0				—Br	28
−90.4	−80.9	Levo	−58.8	—I	29

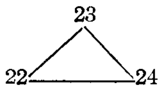
The absolute order of the groups in the lower half of the Table is less certainly known than that in the upper part of the Table. This fact is emphasized by the exception to the first generalization in the configuration of methylphenylcarbinol [Levene and Harris, *J. Biol. Chem.*, **113**, 55 (1936)].

second triangle has at its corners the ordinal numbers 23, 24 and 25, corresponding to methyl, hydroxyl and carboxyl. The passage through the numbers in increasing order is clockwise. If this arrangement corresponds to levorotatory lactic acid then the counterclockwise arrangement corresponds to the enantiomer.

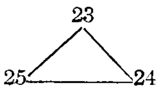
An application of the ordinal numbers of the groups to four secondary carbinols as related configurationally to lactic acid will next be made. The arrangement of the groups in the configurationally related methyl-*n*-propylcarbinol (I), methylisopropylcarbinol (II) and lactic acid (III) would show the following corresponding faces of the three tetrahedra using the ordinal numbers for the groups.



I

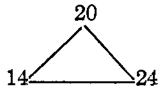


II



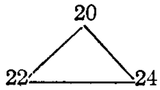
III

All of these numbers increase clockwise. Therefore the three levorotatory compounds have the same configuration. Another case is that of ethyl-*n*-propylcarbinol (IV), ethylisopropylcarbinol (V) and lactic acid (III).



IV

Clockwise

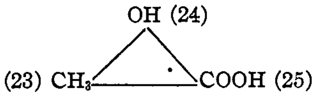


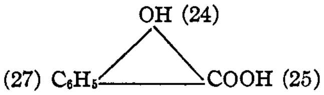
V

Counterclockwise

Thus IV would have the same configuration as the lactic acid of the same rotation while V would have the opposite configuration. In other words, levorotatory IV would have the same configuration as levorotatory lactic acid while dextrorotatory V would have the same configuration as levorotatory lactic acid. Therefore the configurationally related IV and V would have opposite signs of rotation. These deductions regarding the four carbinols agree with the experimental facts as determined by Levene and his collaborators.

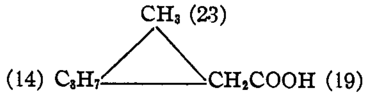
Similarly some three hundred known configurations have been checked successfully by means of the ordinal numbers of the table. No exception has been found to the rule: *If the arrangements of the ordinal numbers in two compounds are both clockwise or both counterclockwise, the two compounds have the same configurations for the same sign of rotation.* Another expression of these relations is as follows: two or more configurationally related substances rotate in the same direction when the ordinal numbers are in the same clockwise or counterclockwise order in both, and rotate in opposite directions when the order in one is opposite to that in the other. The value of such a rule in detecting Walden inversions is obvious.



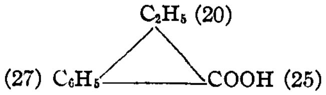


It may be proper to indulge in one speculative application of the rule. No direct chemical means have been found for relating the configurations of lactic and mandelic acids. Applying the rule, we conclude that levorotatory lactic and mandelic acids have the same configuration. Freudenberg[3] has come to the same conclusion from indirect evidence.

Similarly, all three groups may be substituted by other radicals and the configurational relationships of the compounds established as shown by the following.



Dextro
(counterclockwise)



Levo
(clockwise)

The present rule is being applied to the still unsettled problem of the configurational relationships of the secondary carbinols to their halides.

Summary

An empirical table of ordinal numbers has been developed for 29 groups which occur in many optically active carbon compounds. By means of this table the configurational relations of a wide range of compounds can be predicted.

[3] Freudenberg, *Ber.*, **66**, 177 (1933).

STATE COLLEGE, PA. RECEIVED MARCH 11, 1936

[CONTRIBUTION FROM THE INSTITUTE OF EXPERIMENTAL BIOLOGY, UNIVERSITY OF CALIFORNIA]

The Use of the Fractionating Column for the Separation of Fatty Acids[1]

BY SAMUEL LEPKOVSKY, GEORGE V. FESKOV AND HERBERT M. EVANS

Introduction

Although fractional distillation has long been used for the separation of fatty acids, the results have been anything but satisfactory, and in many cases have been decidedly confusing.[2–6]

It is surprising that the fractionating column has found so little use in laboratories engaged in fat analyses. Several such columns have been described. One, described from this Laboratory,[7] has been improved and will be described in detail below. It is useful only when large amounts of fatty acids are to be distilled. A more suitable apparatus for smaller amounts has been described by Bush and Schwartz.[8] Jantzen and Tiedcke[9] have also described a very efficient column for rather small amounts of material.

The fractionating column has undergone intensive development in the last few years, every part of it having received attention—the still head,[10]

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(1) Aided by grants from the Rockefeller Foundation of New York City, Board of Research and the College of Agriculture of the University of California.

(2) H. J. Channon, J. C. Drummond and J. Golding, *Analyst*, **49**, 311 (1924).

(3) C. Crowther and A. Hynd, *Biochem. J.*, **11**, 139 (1917).

(4) E. B. Holland, M. E. Garvey, H. B. Pierce, A. C. Messer, J. G. Archibald and C. O. Dunbar, *J. Agri. Research*, **24**, 365 (1923).

(5) E. B. Holland and J. P. Buckley, *ibid.*, **12**, 719 (1918).

(6) E. F. Armstrong, J. Allan and C. W. Moore, *J. Soc. Chem. Ind.*, **44**, 63T (1925).

(7) H. M. Evans, R. E. Cornish, S. Lepkovsky, R. C. Archibald and G. Feskov, *Ind. Eng. Chem., Anal. Ed.*, **2**, 339 (1930).

(8) M. T. Bush and A. M. Schwartz, *ibid.*, **4**, 142 (1932).

(9) E. Jantzen and C. Tiedcke, *J. prakt. Chem.*, **235**, 277 (1930).

(10) E. C. Wagner and J. K. Simons, *Ind. Eng. Chem., Anal. Ed.*, **5**, 183 (1933).