
Mulliken Samuel Parsons
A METHOD
FOR
THE IDENTIFICATION OF PURE ORGANIC COMPOUNDS

BY A SYSTEMATIC ANALYTICAL PROCEDURE BASED ON PHYSICAL PROPERTIES AND CHEMICAL REACTIONS

VOL. I
CONTAINING CLASSIFIED DESCRIPTIONS OF ABOUT 2300 OF THE MORE IMPORTANT COMPOUNDS OF CARBON WITH HYDROGEN AND WITH HYDROGEN AND OXYGEN

BY
SAMUEL PARSONS MULLIKEN, PH.D.
Instructor in Organic Chemistry and Organic Analysis at the Massachusetts Institute of Technology Boston, Mass.

FIRST EDITION
FIRST THOUSAND

NEW YORK
JOHN WILEY & SONS
LONDON: CHAPMAN & HALL, LIMITED
1904
PREFACE.

At the time of writing the only general and fairly systematic procedure for the identification of previously described organic compounds of all classes is that which may be conveniently designated the Method of the Empirical Formula. In following this procedure a determination of the percentage composition is first made. The molecular weight is next determined or conjectured. From these data an empirical formula is calculated. The properties of the substance are then compared with those of all the known compounds possessing this formula by reference to their scattered literature, for which Richter’s “Lexicon der Kohlenstoff-Verbindungen” with its supplements now furnishes a very complete index. Resting, as it chiefly does, on the two fundamental properties, percentage composition and molecular weight—which alone among the chemical constants can be readily calculated for every compound in advance of its discovery—it is probable that this method will long remain the last resort in all earnest attempts to establish the identity of compounds which have been previously undescribed or very imperfectly characterized through their physical and chemical properties. Nevertheless, when we turn to the great body of well-characterized compounds that occur with some frequency in the products of Nature, the useful arts, and the scientific laboratory, there is good reason to raise the question whether the Method of the Empirical Formula is from the practical standpoint a sufficiently satisfactory one. It is evidently not if any substitute can be found that will lead the analyst to the same results with less expenditure of time and effort, and without requiring unusual knowledge or skill on his part; and it is not to be denied that in these respects this method makes a very poor showing. The indispensable key to its use is proficiency in ultimate organic analysis, whose difficult technique is fully mastered only by long practice. The performance of the combustions, which must be made in duplicate to secure certainty, is at best a time-consuming operation; and even after reliable results have been obtained, it is further necessary, in order to fully identify a compound, to resort to a study of its physical properties, chemical behavior, and perhaps to a molecular-weight determination. The consequence of this has been that the identification of organic compounds by this general method has been practically limited to its occasional employment in laboratories devoted to synthetic organic research, and that such identifications when attempted elsewhere are usually accomplished, often with uncertain results, by the use of disconnected desultory tests. Through these considerations, and with the belief that a path of less resistance could be broken out for the analyst, the writer began more than eight years ago the studies whose first results appear in this volume.
The present method, as contrasted with that just described, gives fuller recognition to the important truths that percentage composition and molecular weight are merely two among many highly significant characteristics of every compound; and that without recourse to them, by the use of the more easily determined properties like qualitative elementary composition, color, melting-point, boiling-point, solubility, specific gravity, alkali neutralizing power, and chemical behavior under prescribed conditions, entirely satisfactory identifications may be made—provided a sufficient number of these facts which are at the disposal of the systematist are carefully verified and suitably coordinated in a classified system.

The new method therefore rests, as will be more fully explained in the introductory chapter, upon a classification designed to secure for the carbon compounds those advantages which have been already so long enjoyed in Botany and other branches of Natural History through the use of systematized descriptions of salient characteristics. The compounds, or chemical "species," have been first grouped into "orders" on the basis of their qualitative elementary composition; then into "genera" (aldehydes, acids, phenols, etc.), usually on the basis of behavior in simple chemical tests; and, finally, arranged within each genus according to the increasing value of some readily-determined constant like the melting-point or boiling-point. The name of each species is followed in the tables by a brief specific characterization enumerating some of the simpler properties of the substance that have genuine analytical significance, and then, whenever possible, by detailed directions for preliminary and corroborative chemical tests which can be performed with small quantities of material.

The phrase "More Important Compounds" used in the title is unavoidably indefinite; but the intention has been to admit all substances to the tables for which there is more than a remote chance that they may come into the hands of the analyst as unknown compounds. Such a list naturally includes: first, all compounds that may be isolated in a state of purity and without excessive difficulty from materials used in the arts, or from substances which occur somewhat abundantly in Nature; second, compounds of minor importance which may easily be formed in the laboratory as by-products in reactions between substances of more common occurrence; third, many rare compounds which have acquired a general scientific interest either on account of their properties or as representatives of peculiar types. Very few compounds that could be purchased in the market in a state of purity have been omitted except through oversight. The most important intentional omissions are: substances whose claims to recognition as distinct chemical species are not generally accepted; uncrystallizable syrups that cannot be distilled without decomposition; the oily and fatty glycerides; those glucosides and synthetic sugars of which specimens could not be obtained for examination.

The claims for admission to this volume of every compound of carbon with hydrogen, or with hydrogen and oxygen, that receives mention in the second edition of Beilstein's great "Handbuch der organischen Chemie" and in its supplements issued prior to January, 1902, have been separately passed upon, and about 2300 selected as deserving mention in the tables. All copied data used in the manuscript sent to the publisher have been twice compared with their source by the author and once by Dr. Heyward Seudder.
Obviously the attempt to establish an analytical system of the proposed character on any less secure foundation than an extended first-hand study of a very large number of representative compounds so selected as to cover all important types, would be to invite the fate of "the foolish man which built his house upon the sand"; for existing descriptions of the reactions of even the most familiar compounds very rarely state the experimental conditions and phenomena in terms that are immediately available for the purposes of a systematic analytical classification. The chemical tests that have been relied upon for arranging the chemical species in genera are therefore the result of many hundred original experiments made upon several hundred compounds in the laboratories of the Massachusetts Institute of Technology, the preparations used being supplied for the most part from the valuable Institute collection. Yet in spite of the considerable labor expended in this way, since it has been physically impossible to examine personally every species described, it would be absurd to deny that some may be wrongly located in the classification. To safeguard the analyst as far as possible against errors arising from such imperfect descriptions, every reasonable precaution that has suggested itself has been taken during the construction of the procedures and tables. The names of those compounds whose generic positions have been established by original experiments in the author's laboratory are distinguished from others by being preceded by the mark †, though it is not true that every property ascribed to a substance thus marked is necessarily an original or guaranteed datum. Of the "numbered specific tests" it may, however, be said that each one has been performed at least several times in accordance with the directions contained in the manuscript; that they have all been used on more than one occasion; and that they have proved successful in the hands of two or more persons.

The specific characterizations are all quite brief because the work is intended to be used as a compact practical analytical guide and index, and not as a handbook of descriptive Organic Chemistry; and because the value of a specific description to the analyst never increases, beyond a certain point, directly in proportion to the number of properties and tests included—long descriptions often becoming unwieldy and confusing through suggesting too many alternatives of unequal merit.

To obtain all the new material required for these pages single-handed would have proved a disheartening labor. The writer's grateful acknowledgments are therefore due to the many friends (most of whom are or have been connected with the chemical department of the Massachusetts Institute of Technology) who have rendered assistance in the work. Some of the most important contributions from this source are recorded in the unpublished "thesis" investigations of the writer's students. Valuable information has thus been furnished by Messrs. A. P. Norris, C. L. M. Pettee, H. M. Loomis, H. Seudder, B. R. Rickards, A. R. S. Booth, J. W. Brown, J. R. Odell, and Misses E. M. Chandler and A. F. Blood. The writer has also been ably assisted at different times by Dr. Paul Chapin and Messrs. A. C. Davis and Herbert Walker. To his friend, Dr. Heyward Seudder, the author's thanks are however especially due for generous and untiring cooperation during a considerable part of this undertaking. Many of the best methods, particularly among the "specific tests," are the fruits of his research, or have been improved
in consequence of his suggestions, while nearly the whole of the manuscript, as well as the proof-sheets, have received the benefit of his criticism. It is regretted that the necessary practice of omitting, for the sake of simplicity and compactness in tabulation, those bibliographical references which, while they have aided the writer, would not be of positive advantage to the analyst, has prevented that full acknowledgment of aid from many earlier investigators that would otherwise have been gladly rendered.

In closing, a word should be added in regard to the proposed extension of this method to the other organic compounds. Preliminary investigations on the identification of the carbon compounds containing nitrogen, or nitrogen and oxygen, were begun about three years ago, and are still in progress. This second part of the work is now well advanced, and, when completed, it is intended to publish the results as Vol. II of the Method under the joint authorship of the writer and Dr. Heyward Scudder. A third volume to provide for the compounds of carbon with the remaining most important elements will then perhaps follow. The compounds described in the second volume will constitute Order II of the analytical system. It is desired to base all the most essential portions of the descriptions of at least several hundred of these species on original or personally verified data, as it is only in this way that a thoroughly satisfactory result can be assured. The enterprise is a laborious one, and as many of these compounds can not be purchased, and the necessity of preparing them all in the writer's laboratory would cause much delay, it is hoped that other organic chemists may be willing to coöperate in the work to the extent of placing at the author's disposal small samples of any of the less accessible nitrogen compounds which they may have prepared or collected.

S. P. M.

Massachusetts Institute of Technology, December, 1903.
# CONTENTS

<table>
<thead>
<tr>
<th>PAGES</th>
<th>TABLES</th>
<th>CHAPTERS</th>
</tr>
</thead>
<tbody>
<tr>
<td>iii–vi</td>
<td>xi–xii</td>
<td>I–III, V–VII</td>
</tr>
</tbody>
</table>

## CHAPTER I.

**Classification of Compounds and the Analytical Procedure.**

- *Explanation of Classification.*—Orders, Genera, Divisions, Sections, Species, 1–2.
- *General Directions for Examination of Unknown Compounds.*—Evidences of Homogeneity; Examination of Physical Characteristics; Determination of Order; Determination of Genus; Tabular Summary of Generic Tests; Determination of Division and Section; Determination of Species. 3–7.
- *Examples illustrating the Analytical Procedure.* 7–8.

## CHAPTER II.

**Ordinal Tests.**

- *Procedure for Detection of the Elements in Organic Compounds.*—Carbon and Ash Constituents; Sulphur, Nitrogen, and the Halogens; Ignition with Sodium; Sulphur; Nitrogen; Nitrogen and Sulphur together; Phosphorus; Halogens; Iodine; Bromine; Chlorine.

## CHAPTER III.

**Genus I (Subord. I, Ord. I).—Aldehydes.**

- *Generic Characterization.*—Generic Test I; Observations on Test; Aldehyde Characteristics. 15–16.
- *Numbered Specific or Semi-specific Aldehyde Tests.*—(101)* Compounds reducing Tollen's Reagent; (111) Acetaldehyde; (112) Acrolein; (113) Benzaldehyde; (114) Formic Aldehyde; (115) Furfurol. 22–25.

## CHAPTER IV.

**Genus II (Subord. I, Ord. II).—Carbohydrates.**

- *Generic Characterization.*—Generic Test II; Generic Subdivisions; Carbohydrate Characteristics. 26–28.
- *Analytical Tables.*—Section 1 (Soluble Species), 29; Section 2 (Insoluble Species), 31.
- *Numbered Sectional and Specific Carbohydrate Tests.*—(201) Osmazone Precipitations; (202) Reduction of Fehling's Solution; (203) Furfurol; (204) Phloroglucine Reaction; (205) Oxidations to Mucic or Saccharic Acids. 32–34.

*The numerals in parentheses refer to test numbers—not pages.
CONTENTS.

CHAPTER V.

GENUS III (SUBORD. I, ORD. I).—ACIDS. ........................................... 35-86

Generic Characterization.—Generic Test III; Observations on Test; Acid Characteristics; Generic Subdivisions. 35-38.

Analytical Tables.—Div. A, Sec. 1 (Solid Soluble Species), 39; Div. A, Sec. 2 (Solid but not Soluble Species), 62; Div. B, Sec. 1 (Liquid Soluble Species), 73; Div. B, Sec. 2 (Liquid but not Soluble Species), 75.

Numbered Specific or Semi-specific Tests.—(301) Neutralization Equivalent; (302) α-Oxoyacids; (303) Acids losing Carbon Dioxide at 200; (304) Unsaturated Acids; (305) Esters with characteristic Odors; (306) Metallic Salts; (307) Acid Anhydrides of Genus III; (311) Acetic, Propionic, Butyric, and Isobutyric Acids; (312) Benzoic Acid; (313) Cinnamic Acid; (314) Citric, Malic, and Tartaric Acids; (315) Formic Acid; (316) Glutaric Acid; (317) Oxalic Acid; (318) Phthalic Acid, Isophthalic Acid and Terephthalic Acid; (319) Salicylic Acid; (320) Succiinic Acid. 77-86.

CHAPTER VI.

GENUS IV (SUBORD. I, ORD. I).—PHENOLIC COMPOUNDS. .................. 87-110

Generic Characterization.—Generic Test IV. Observations on Test; Phenolic Characteristics. 87-90.

Analytical Tables.—Div. A (Solid Species), 91; Div. B (Liquid Species), 104.

Numbered Specific or Semi-specific Tests.—(401) Ferric chloride Colorations; (402) Pthalene Fusion; (411) Hydroquinone; (412) α-Naphthol; (413) β-Naphthol; (414) Phenol; (415) Phloroglucine; (416) Pyrocatechol; (417) Pyrogallol; (418) Resorcin; (419) Thymol. 107-110.

CHAPTER VII.

GENUS V (SUBORD. I, ORD. I).—ESTERS ........................................... 111-127

Generic Characterization.—Generic Test V, 111; Saponification and Saponification Equivalent (Rapid Method), 111; Saponification to obtain both Acid and Neutral Products (Longer Method), 113; Examination of the most Important Neutral Saponification Products, 113; Examination of the Acid Products, 116; Observations on Test V. 117.

Analytical Tables.—Div. A (Solid Esters), 118; Div. B (Liquid Esters), 120.

CHAPTER VIII.

GENUS VI (SUBORD. I, ORD. I).—ACID ANHYDRIDES AND LACTONES. .......... 128-132

Generic Characterization, 128.

Analytical Tables.—Div. A (Solid Species), 129; Div. B (Liquid Species), 131.

CHAPTER IX.

GENUS VII (SUBORD. I, ORD. I).—KETONES ................................... 133-150

Generic Characterization.—Generic Test VII; Procedures 1 and 2; Observations on the Test. 133-135.

Analytical Tables.—Div. A (Solid Species), 136; Div. B (Liquid Species), 141.

Numbered Specific or Semi-specific Ketone Tests.—(701) Colorations with Sodium Nitroprusside; (702) Oxidations with Chromic Acid; (703) Pyroly-red Reaction of γ-Diketones; (711) Acetone; (712) Acetophenone; (713) Benzoin; (714) Benzophenone; (715) Camphor. 146-150.
CONTENTS.

CHAPTER X.

Genus VIII (Subord. I, Ord. I).—Alcohols .......................................................... 151-172
 Generic Characterization.—Generic Test VIII; Procedures 1, 2, and 3; Observations
 on the Test. 151-154.
 Analytical Tables.—Div. A, Sec. 1 (Solid "Soluble" Species), 155; Div. A, Sec. 2
 (Solid and not "Soluble" Species), 158; Div. B (Liquid Species), with Sp. Gr.
 less than 0.90, 160; Div. B, Sec. 2 (Liquid Species, with Sp. Gr. greater than
 0.90), 164.
 Numbered Specific or Semi-specific Tests.—(S01) The Iodoform Test; (S11) Allyl
 Alcohol; (S12) Benzyl Alcohol; (S13) Butyl Alcohol; (S14) Ethyl Alcohol;
 (S15) Ethylene Glycol; (S16) Glycerine; (S17) Isobutyl Alcohol; (S18) Iso-
 propyl Alcohol; (S19) Methyl Alcohol; (S20) Propyl Alcohol. 166-72.

CHAPTER XI.

Genus IX (Subord. I, Ord. I).—Hydrocarbons, etc ............................................. 173-203
 Analytical Tables.—Div. A (Solid Species), 174; Div. B, Sec. 1 (Liquid Species
 Sp. Gr. below 0.85, not giving Tests 901-903), 182; Div. B, Sec. 2 (Liquid Speci-
 es, Sp. Gr. below 0.85, but attacked in Tests 901, 902, or 903), 184; Div. B,
 Sec. 3 (Liquid Species, Sp. Gr. above 0.85), 189.
 Numbered Specific or Semi-specific Tests.—(901) Bromine Test for Unsaturated,
 etc.; (902) Action of Fuming Sulphuric Acid; (903) Action of Fuming Nitric
 Acid; (904) Colorations with Aluminium Chloride; (905) Oxidation of Side-
 chains (1) with Permanganate, (2) with Chromic Acid, (3) with Nitric Acid;
 (906) Test for C=CH Group; (907) Saturated Esters of Div. B; (911) Ace-
 naphthene; (912) Anthracene; (913) Benzene; (914) Mesitylene; (915) Naphtha-
 lene; (916) Phenanthrene; (917) Pseudocumene; (918) Toluen; (919) m-Xylene;
 (920) p-Xylene; (921) o-Xylene, 195-203.

CHAPTER XII.

Suborder II of Order I.—Colored Compounds of Order I ..................................... 204-216
 Subordinal Characterization, 204.
 Analytical Tables.—Div. A, Sec. 1 (Solid Species of Determined Melting-point), 205;
 Div. A (Supplementary), Sec. 2, 212; Div. B (Liquid Species), 215.
 Numbered Specific Tests.—No. 1011, Anthraquinone; 1012, Benzoinone; 1013,
 α-Naphthoquinone; 1014, Phenanthrenequinone, 216.

CHAPTER XIII.

Special Methods, Apparatus, and Reagents ....................................................... 217-237
 Melting and Boiling-points.—Usual and Special Methods for Determining; Sources
 of Error and Corrections, 217-223.
 Thermometric Indications of Chemical Purity.—Fractionation Tests; Sharpness Tests;
 Fusion and Boiling Intervals. 223-227.
 Specific Gravities.—Determination with the Capillary Pyrometer or the Pipette,
 227-229.
 Color.—Color Terminology; Pigmentary Color Standards; Color Symbols; Color
 Comparisons, 230-234.
CONTENTS.

The Manipulation of Small Quantities.—Solid Precipitates: Liquids. 234–236
List of Special Reagents and Apparatus, 236–237.

Alphabetical Index. .......................................................... 239–243
Formula Index. ................................................................. 244–264
Color Standard. ................................................................. In the back cover.