SPECTRAL DATA OF NATURAL PRODUCTS

VOLUME I

K. YAMAGUCHI

SPECTRAL DATA OF NATURAL PRODUCTS

VOLUME I

K. YAMAGUCHI

Torii & Co., Ltd.,
Nihonbashi, Tokyo, Japan

ELSEVIER PUBLISHING COMPANY
Amsterdam London New York
1970

ELSEVIER PUBLISHING COMPANY
335 Jan van Galenstraat
P. O. Box 211, Amsterdam, The Netherlands

ELSEVIER PUBLISHING CO. LTD.
Barking, Essex, England

AMERICAN ELSEVIER PUBLISHING COMPANY, INC.
52 Vanderbilt Avenue
New York, New York 10017

Library of Congress Card Number: 72-105623
Standard Book Number: 444-40841-X

Preface

In the late 1950's, the chemistry of natural products underwent a dramatic change as regards the methods of structure determination. This change has as its direct basis the recent developments in electronics, and completely upset the classical chemical methods of recognizing unsaturation, functional groups and even the carbon skeleton. The techniques which played the most important role in this revolution were various spectroscopic methods: UV, IR, NMR, ORD, CD and MS, and more recently NMDR and NOE as well as X-ray analysis. Applying these techniques, organic chemists have elucidated the structures of various natural products with the most extraordinary and fascinating structures, which had never been dreamed of by any classical chemist.

The usefulness of these methods naturally prompted the publication of a number of instructive books and collections of spectra, large and small, on all of these methods. To the author's knowledge, however, no collective book has been published which classifies natural products according to structural type, and presents them with the spectral data used for their structure determination. The reason for attempting the present series is that such a systematic collection should be of great help for chemists working in this field.

It consists of two volumes; the first one deals with the compounds whose structures were elucidated before 1963, and the second those structures which were determined in 1964 and 1965. In each volume the natural products are classified into 20 groups according to their structure types. The structure, available physical constants and absorption spectral data (UV, IR, NMR, MS, ORD and CD) of each compound are presented, together with their natural origin and the relevant literature references. The second volume carries, in addition, an Appendix listing the natural origins and references for the compounds whose structures were reported during 1966-1968.

Throughout the preparation, the author felt hopelessly aware of the limitation of what one individual can achieve for this kind of classification and collection, in spite of his volition and effort. Now he, a Don Quixote in 1969, has to confess to himself that, if this kind of collection is needed in the future for the further development of the chemistry of natural products, it can and should be done only by the co-operation of several specialists, using an electronic computer.

The major part of these books was completed in 1966 during the author's previous position at the National Institute of Hygienic Sciences, and the

Appendix was collected at the Research Laboratories, Torii & Co., Ltd., where the author is currently working.

Many colleagues helped in all directions, and the author particularly acknowledges the encouragement of Emeritus Professor Tatsuo Kariyone, the previous Director of the National Institute of Hygienic Sciences, and Professor Shô Itô, of Tohoku University. He is indebted to Professor Hiroshi Ageta, Showa College of Pharmacy; Dr. Shinsaku Natori, Head of the Pharmacognosy Division, National Institute of Hygienic Sciences; and to Dr. Mitsuaki Kodama, Department of Chemistry, Tohoku University, for their helpful advice and meticulous reading and correction of the manuscript. Thanks are also due to Mr. Setsuo Hirokawa, the Managing Director of Hirokawa Publishing Co., and Mr. Takashi Torii, the President of Torii & Co., Ltd., for their help which enabled this book to appear.

JUNE 1969 K. YAMAGUCHI

Abbreviations for the names of periodicales

Acta Chem. Scand.	Acta chemica Scandinavica
Agr. Biol. Chem. Japan	Agricultural and Biological Chemistry (Japan)
Angew. Chem.	Angewandte Chemie
Ann.	Justus Liebigs Annalen der Chemie
Arch. d. Pharm.	Archiev der Pharmazie und Berichte der deutschen pharmazeutischen Gesellschaft
Austr. J. Chem.	Australian Journal of Chemistry
Ber.	Chemische Berichte
Biochem. J.	The Biochemical Journal
Bull. Chem. Japan	Bulletin of the Chemical Society of Japan
Bull. soc. chim. France	Bulletin de la Sociētē Chimique de France
C. A.	Chemical Abstracts
Canad. J. Chem.	Canadian Journal of Chemistry
Chem. & Ind.	Chemistry and Industry (London)
Chem. Pharm. Bull. Japan	Chemical and Pharmaceutical Bulletin (Tokyo)
Collection Czech. Chem. Comm.	Collectiòn of Czechosolovak Chemical Communication
Experientia	Experientia
Helv.	Helvetica Chimica Acta
J. A. C. S.	The Journal of American Chemical Society
J. Biol. Chem.	The Journal of Biological Chemistry
J. C. S.	Journal of Chemical Society (London)
J. Indian Chem. Soc.	Journal of the Indian Chemical Society
J. Org. Chem.	The Journal of the Organic Chemistry
J. Pharm. Sci.	Journal of Pharmaceutical Sciences
Kashi	Nippon Kagaku Zasshi (日本化学雑誌)=Journal of the Chemical Society of Japan
Nature	Nature
Naturwissenschaften	Die Naturwissenschaften
Nôgeishi	Nippon Nôgei-Kagaku Kaishi (日本農芸化学会誌)=Journal of the Agricultural Chemical Society of Japan
Phytochem.	Phytochemistry
Proc. Chem. Soc.	Proceedings of the Chemical Society (London)
Tetrahedron	Tetrahedron
Tetrahedron Letters	Tetrahedron Letters
Y. Z.	Yakugaku Zasshi (薬学雑誌)=Journal of the Pharmaceutical Society of Japan

Other periodicals are referred to Chemical Abstracts and Nihon Kagaku Sôran (日本化学総覧) and abbreviated by the system of Chemical Abstracts.

CONTENTS

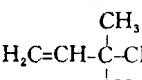
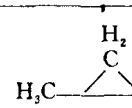
1 Hydrocarbons and the Derivatives

[A] NMR Spectra

(1) Chemical shifts of protons are indicated in Table 1[1]

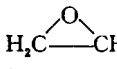
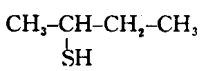
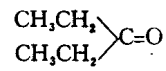
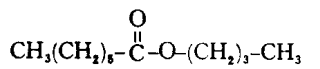
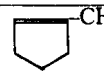
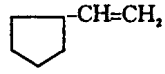
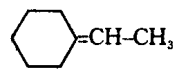
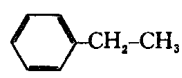
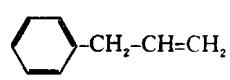
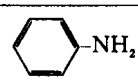
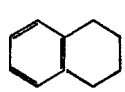
Table 1 (Jungnickel *et al.*)[1]

Sample in 30% CCl_4 solv., sweep rate to 10 cps/s, δ=ppm to TMS (internal reference)

Compound	Proton of	Chem. shift δ
	=CH—	5.75
	$=CH_2$	4.83
	$-CH_3$	1.00
CH_3-CH=CH-CH_2-CH_2-CH_2-CH_3	=CH—	5.3
	$-CH_3$, $-CH_2-$	0.9~1.9
$HC\equiv C$-CH_2-CH_3	$\equiv C$-CH_2—	2.17
	$\equiv CH$	1.78
	$-CH_3$	1.14
	$-CH_3$	1.03
	ring—CH_2—	0.25
CH_3-CH_2-OH	—OH	4.90
	$-CH_3$	1.17
	$-CH_2-$	3.60
CH_3-CH_2-CH_2-CH_2-OH	—OH	4.7
	—O-CH_2—	3.5
	$-CH_3$, $-CH_2-$	0.8~1.7

1) Jungnickel, J.Z *et al*: *Anal. Chem.*, **35**, 938 (1963).

1 Hydrocarbons and the Derivatives

Compound	Proton of	Chem. shift δ
$(CH_3-CH_2-CH_2-)_2O$	$-CH_2-O-$ $\beta-CH_2-$ CH_3-	3.30 1.50 0.90
$(CH_3-CH_2-CH_2-CH_2-)_2O$	$-CH_2-O-$ CH_3-, $-CH_2-$	3.3 0.9~1.4
	$-CH_2-O-CH-$ $-CH_3$	2.2~2.8 1.22
	$-S-CH$ $-SH$, $-CH_3$, $-CH_2-$	2.83 0.9~1.6
$CH_3-S-CH_2-CH_2-CH_3$	$S-CH_2-$ CH_3-S, $-CH_2-CH_3$	2.4 0.9~2.0
	$-CO-CH_2-$ $-CH_3$	2.35 1.0
	$-CO-O-CH_2-$ CH_3-, $-CH_2-$	4.00 0.9~2.2
	$=CH-$ CH_3-, $-CH_2-$	5.20 1.7~2.2
	$=CH-$ $=CH_2$ $-CH_2-$, $>CH-$	5.66 4.83 1.5~2.4
	$=CH-$ CH_3-, $-CH_2-$	5.05 1.5~2.1
	Arom. H Ar. $-CH_2-$ $-CH_3$	7.05 2.53 1.15
	Arom. H $=CH-$ $=CH_2$	7.05 5.8 5.0
	Arom. H Ar. $-NH_2$	6.3~7.2 3.3
	Arom. H $\alpha-CH_2-$ $\beta-CH_2-$	6.85 2.60 1.66
	$\alpha-CH_2-$ $\beta-CH_2-$, $>NH$	2.84 1.5~1.8

(2) **Approximate τ values of various protons** are indicated in Table 2

Table 2 (Jones, R.A.Y *et al.*[1a])

Atomic Group	τ	Atomic Group	τ
CH_3-C	9.1	CH_3-O	6.7
C-CH_2-C	8.5~8.8	Ar-NH_2	6.5
C-CH-C (C)		CH_3-O-CO	6.2
C-NH_2	8.4	CH_3-O-Ar	6.2
CH_3-C=C	8.2	H_2C=C	5.3
CH_3-C=O	8.0	H-C=C (C)	4.7
CH_3-S	8.0	C-OH	4.7
CH_3-N	7.8	CO-NH_2	3.0
H-C≡C	7.7	H-Ar	2~3
CH_3-Ar	7.6	Ar-OH	2.3
CH_3-N-CO (N)	7.2	CHO	0.2
		COOH	−0.8

(3) **Typical coupling constants** are indicated in Table 3

Table 3 (Jones, R.A.Y *et al.*)

Group	*J*ab (c/s)	Group	*J*ab (c/s)
C(Ha)(Hb)	12~15	Ha>C=C<Hb	11~18
Ha-C-C-Hb	8~12	Ha>C=C<Hb	6~14
Ha-C-C-Hb	2~4	Ha>C=C<CHb	0.5~2
Ha-C-C-C-Hb	0	Ha>C=C<CHb	0

1a) Jones, R.A.Y *et al*: *Chem. & Ind.*, **1962**, 522.

[B] Saturated Hydrocarbons and Plant Waxes

(1) Mass Spectra of Saturated Hydrocarbons

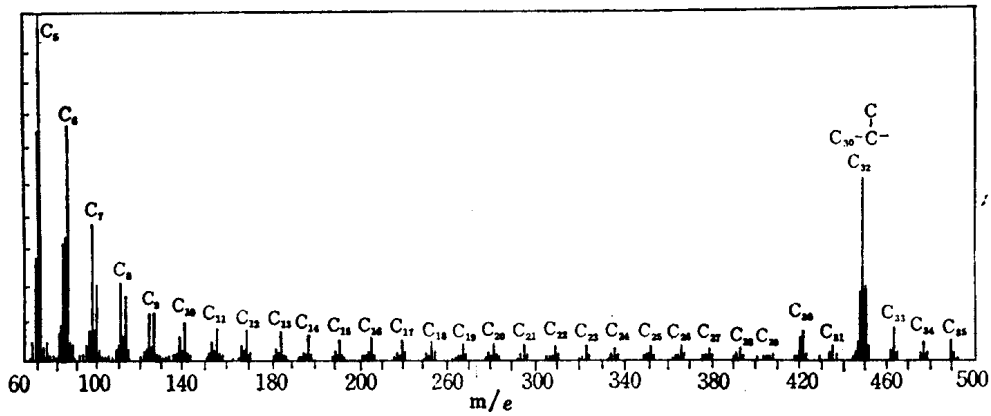


Fig. 1 Phthiocerane (3-Methyltetratriacontane)[1b] (Biemann, K)

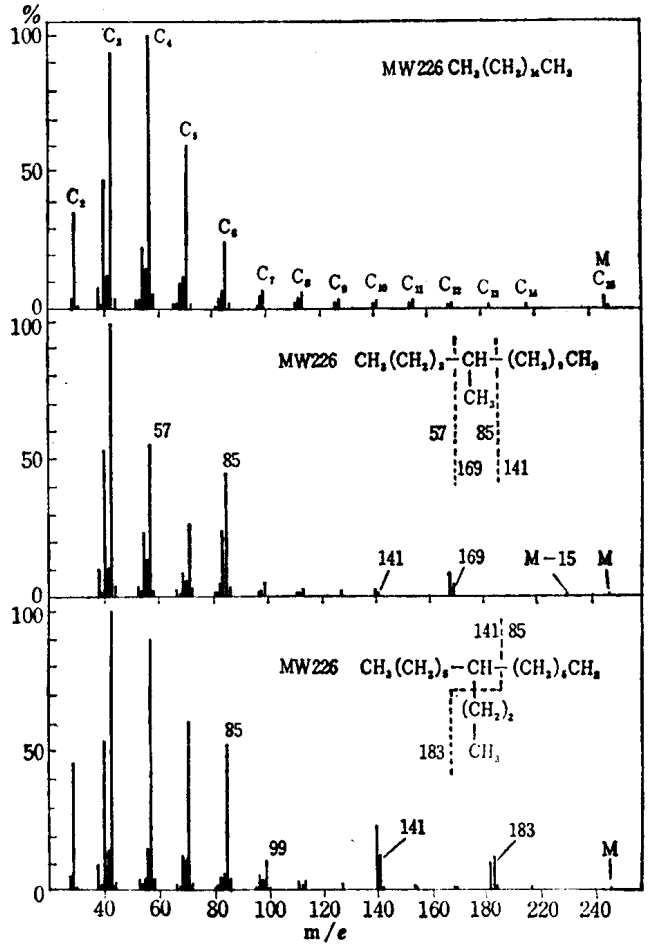


Fig. 2 Three isomeric Hydrocarbons $C_{16}H_{34}$[1c] (Schumacher, E)

1b) Biemann, K: *Angew. Chem.*, **74**, 102 (1962).

1c) Schumacher, E: *Helv. Chim. Acta*, **46**, 1295 (1963).

(2) Mass spectra of vegetable paraffins and primary alcohols[1d]

(3) Eicosan-1-ol, docosan-1-ol, octacosan-1-ol, tricontan-1-ol and, octadecanoic, eicosanoic, docosanic, tetracosanoic, hexacosanoic, octacosanoic, triacontanoic and dotriacontanoic acids from the heart wood of ***Vitex divaricata***[2].

(4) *n*-Alkanes from tridecane to tetracosane, palmitic and stearic acids, β-amyrin, diterpenoids and α-spinasterol from the heart wood of *Manikara bidentata*[3]

〔C〕 Naturally Occurring Polyyne Compounds

(1) Hydrocarbons

(a) Capillene CH_3-C≡C-C≡C-CH_2-C_6H_5 (I)

≪Occurrence≫ *Artemisia capillaris*[4], *A. dracunculus* L. and *Chrysanthemum frutescens* L.[5]

UV λ_{max} mμ (logε): 239, 253 (2.73, 2.63)[4]

IR $V_{max}cm^{-1}$: 2270, 2210, 2160, 1960, 1600, 1500, 1380, 1075, 730, 695[4]

(b) Benzyldiacetylene HC≡C-C≡C-CH_2-C_6H_5 (II)

≪Occurrence≫ *Artemisia frutescens* L.[5] bp. $_{0.01}$ 45~50°, n^{22}1.5726

UV λ_{max}^{Hexane}mμ(ε): 267, 263.5, 257, 252, 247, 238.5, 226, 206.5, 196 (115, 184, 270, 400, 310, 560, 660, 12000, 19000)[5]

(c) Aethusin H_3C-CH=CH-$(C\equiv C)_2$-$(CH=CH)_2$-CH_2-CH_3 (III)

≪Occurrence≫ *Aethusa cynapium* L.[6], mp. 23°, Colorless oil

UV (see Fig. 3), IR (see Fig. 4).

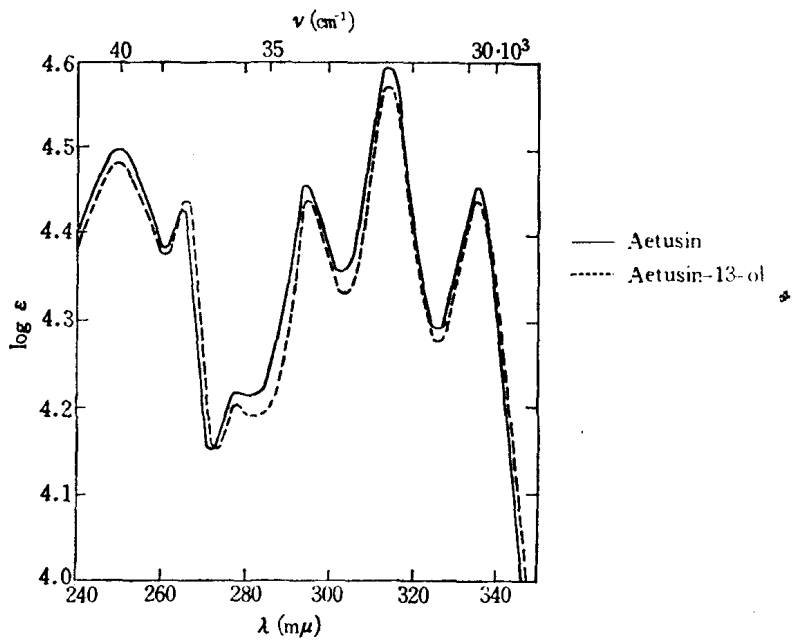


Fig. 3

1d) Waldon, J. D *et al*: *Biochem. J.*, **78**, 435 (1961).
2) Cocker, W *et al*: *Soc.*, **1962**, 5194. 3) Cocker, W *et al*: *ibid.*, **1963**, 677.
4) Harada, R: *J. Chem. Soc. Japan*, **78**, 1031 (1957). 5) Bohlmann, F *et al*: *Ber.*, **95**, 39 (1962).
6) Bohlmann, F *et al*: *ibid.*, **93**, 981 (1960).

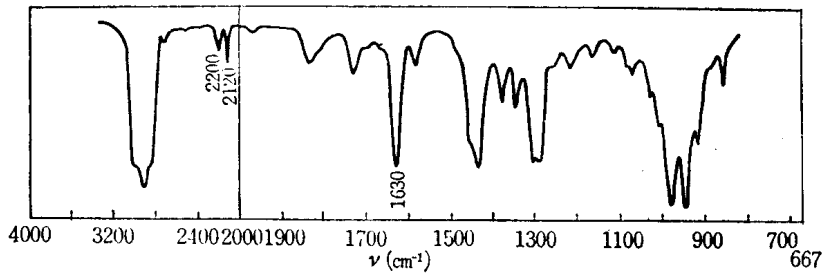


Fig. 4

(d) Tetraynediene[7] $H_3C-CH=CH-(C\equiv C)_4-CH=CH_2$ (IV)

≪Occurrence≫ *Centaurea cyanus* L. and other *Centaurea* spp., mp. 87°,

UV $\lambda_{max}^{Et_2O}$ mμ: 389.5, 360.5, 336, 314.5, 287, 271, 258

IR $\nu_{max}^{CCl_4}$ cm⁻¹: 2190, 2120 (—C≡C—), 1850, 965, 925 (—CH=CH_2), 1615, 945 (—CH=CH—)

(e) Hydrocarbon[7] $H_3C-CH=CH-(C\equiv C)_2-(CH=CH)_2-(CH_2)_4-CH=CH_2$ (V)

≪Occurrence≫ *Centaurea ruthenica* LAM.

UV, IR.

(f) Centaur X_4[8] $H_3C-CH=CH-(C\equiv C)_2-(CH=CH)_2-(CH_2)_4-CH=CH_2$ (VI)

≪Occurrence≫ *Centaurea ruthenica* L., (*trans* compound) mp. 28.5~29.5°

UV $\lambda_{max}^{Et_2O}$ mμ(ε): 336, 314, 296, 279.5, 266, 250.5 (36300, 43400, 32050, 19650, 32800, 41000)

IR $\nu_{max}^{CCl_4}$ cm⁻¹: 1820, 1630, 912 (-CH=CH_2), 1625, 945 (-CH=CH-), 980 (—(CH=CH)$_2$—*trans*), 2190, 2115 (—C≡C—)

(g) Tridecatriyne-(7, 9, 11)-triene-(1, 3, 5)[9] (VII)

$H_3C-(C\equiv C)_3-CH=CH-CH=CH-CH=CH_2$

≪Occurrence≫ *Achillea ptarmica* and other *Achillea* spp.; *Anthemis* spp., mp. 88~93°

UV $\lambda_{max}^{Et_2O}$ mμ: 356, 331, 311, 283

IR ν_{max} cm⁻¹: 2240 (—C≡C—), 1610, 1007 ((CH=CH_2), 1830, 910 (—CH=CH_2), 1385 (≡C-CH_3)

(2) Alcohols and their Acetates

(a) Centaur X_2[7]

$$H_3C-CH=CH-(C\equiv C)_2-(CH=CH)_2-CH_2-\underset{\displaystyle OCOCH_3}{CH}-(CH_2)_2-OCOCH_3 \quad \text{(VIII)}$$

≪Occurrence≫ *Centaurea macrocephala*, mp. 54~56°, $[\alpha]_D$ −5° (MeOH)

UV[7], IR $\nu_{max}^{CHCl_3}$ cm⁻¹: 2190, 2125 (—C≡C—), 1615, 945 (—CH=CH—), 980 ((CH=CH_2), 1725, 1375, 1240 (—OAc)

[Compounds] $H_3C-CH=CH-(C\equiv C)_3-CH=CH-\underset{\displaystyle R_2}{CH}-CH_2-OR_1$ (IX)

(b) 12, 13-Diacetoxytridecadiene (2, 10)-triyne-(4, 6, 8)[7][8] (IX) R_1=Ac, R_2=OAc

≪Occurrence≫ *Centaurea ruthenica* LAM., mp. 64°[7], 76°[8], $[\alpha]_D$ +102.2° ($CHCl_3$)[7]

UV[7] $\lambda_{max}^{Et_2O}$ mμ (ε)[8]: 354.5, 330, 309, 290, 267, 255, 246, 235 (20400, 27800, 20900, 12400, 60400, 75800, 72900, 52000)

7) Bohlmann, F: *Ber.*, **91**, 1631, 1642 (1958). 8) Bohlmann, F *et al*: *ibid.*, **92**, 1319 (1959).
9) Bohlmann, F *et al*: *ibid*, **95**, 1315 (1962).