

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

COPYRIGHT © 1970 BY HIROKAWA PUBLISHING COMPANY, INC. Tokyo

All Rights Reserved. This book or any part thereof may not be reproduced in any form, including photostatic or microfilm form, without written permission from the publishers Hirokawa Publishing Company, Hongo-3, Bunkyo-ku, Tokyo. Printed in Japan.

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 periodicals

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.	Archiv 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 Société 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.	Collection of Czechoslovak 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	1
	A NMR Spectra	1
	B Saturated Hydrocarbons and Plant waxes	4
	C Naturally Occurring Polyene Compounds	5
	D Naphthalene and Phenanthrene Derivatives	18
2.	Carboxylic Acids	20
	A UV Spectra	20
	B IR Spectra.....	20
	C Miscellaneous	20
3.	Amino Acids	25
	A UV Spectra	25
	B IR Spectra.....	25
4.	Acid amides	32
	A UV Spectra	32
	B IR Spectra.....	33
	C Naturally Occurring <i>N</i> -Isobutylpolyene amides	34
	D Miscellaneous	36
5.	Carbohydrates, Uronic Acids and Related Compounds	40
	A UV Spectra	40
	B IR Spectra.....	40
	C Relationship between the Stereochemical Structures and the NMR Spectra of α - and β -Acetylpyranoses	43
	D Mass Spectra of Acetates of methylated Pentoses and Hexoses	46
	E Five-membered Sugar-lactones	49
6.	Glycosides	50
	A Cycas Glycosides	50
	B Thio Glycosides	51
	C Iridoids	52
	D Phenolic Glycosides.....	57
	E Stilbene Glycosides	61
	F Coumarins, Furocoumarins and their Glycosides	63
	G Chalcone and Flavanone Glycosides.....	74

H	Anthocyan and Anthochlor Pigments	86
I	Flavones and Flavone Glycosides	87
J	Chromones, Chromanes, Xanthones and their Glycosides...	104
K	Rotenoids	115
L	Coumaranochroman Derivatives	120
M	Pyrane Derivatives	123
N	Tannins	124
7.	Triterpenoids	130
A	UV Spectra	130
B	IR Spectra	132
C	NMR Spectra	142
D	Mass Spectra	146
E	Oleanane-series Triterpenoids	151
F	Ursane-series Triterpenoids	158
G	Friedelane, Bauerane-series Triterpenoids	161
H	Lupane-series Triterpenoids.....	164
I	Hopane-series Triterpenoids	165
J	Tetracyclic Triterpenoids	169
K	Onocerane-series	180
L	Miscellaneous	181
8.	Steroids	183
A	UV Spectra and Color Reaction	183
B	IR Spectra	186
C	NMR Spectra	191
D	Mass Spectra	195
E	ORD and Gas Chromatography.....	199
F	Sterols	200
G	C ₂₁ -Steroids	206
9.	Steroidal Sapogenins	212
A	UV Spectra	212
B	IR Spectra	212
C	NMR Spectra	215
D	3-Hydroxysapogenins	216
E	1,3-Dihydroxysapogenins	217
F	2,3-Dihydroxysapogenins	219
G	3,12-Dihydroxysapogenins	220
H	3,15-Dihydroxysapogenins	221
I	3,11(2)-Di(Tri)hydroxysapogenins	221
J	1,2,3-Trihydroxysapogenins	222
K	2,3,15-Trihydroxysapogenins.....	223
L	1,2,3,5,-and 1,3,4,5-Tetrahydroxysapogenins	223
M	Pentahydroxysapogenins	224
N	Aromatic Sapogenins.....	225

	O 12-Ketosapogenins.....	225
10.	Cardenolides 227	
	A UV Spectra	227
	B IR Spectra	229
	C Mass Spectra	231
	D Cardenolides	232
	E Bufadienolides	272
11.	Diterpenoids 278	
	A Hydrocarbons	278
	B Alcohols	282
	C Phenols	287
	D Oxides	291
	E Diterpenoid Quinones	292
	F Aldehydes and Ketones	295
	G Resinic acids	299
	H Diterpenoid Lactones	309
	I Furano-terpenoids and Tetranortriterpenoids	316
	J Pyrano-terpenoids	326
12.	Sesquiterpenes 327	
	A UV Spectra	327
	B IR Spectra	327
	C Hydrocarbons and Azulenes	327
	D Alcohols	336
	E Ethers and Furano Compounds	345
	F Aldehydes and Ketones	356
	G Carboxylic Acids	363
	H Lactones	365
13.	Non-terpenic Essential Oils and Isoprenoides 384	
	A UV Spectra	384
	B IR Spectra	385
	C Mass Spectra of Terpenic Hydrocarbons	389
	D Hydrocarbons.....	394
	E Phenols	394
	F Alcohols	394
	G Ketones	395
	H Pyrane Derivatives	399
	I Lactones	400
14.	Pyrethroids 403	
	A UV Spectra	403
	B IR Spectra	404
	C Pyrethrins	404

15.	Constituents of Male-fern and Hop-corn	405
	A UV Spectra	405
	B IR Spectra	405
	C Constituents of Male-fern	405
	D Constituents of Hop-corn	406
16.	Phenolic Substances	407
	A Phenols and Naphthols	407
	B Marihuana Substances	411
	C Tropolones	412
17.	Quinones	415
	A The Quinones described in other Items	415
	B UV Spectra	416
	C IR Spectra	416
	D Benzoquinones	417
	E Naphthoquinones	425
	F Anthraquinones	430
18.	Lignoids	439
	A UV Spectra	439
	B IR Spectra	439
	C Classification by Freudenberg <i>et al.</i>	440
	D Reviews	440
	E Precursor or Model Compounds of Lignin	441
	F Butanolides	449
	G 3,7-Dioxabicyclo-(3,3,0)-octanes	450
	H Lignanes	456
	I Cyclolignanes	457
	J Miscellaneous	462
19.	Carotenoids	464
	A UV Spectra	464
	B IR Spectra	467
	C Natural and Synthetic Carotenoids	467
20.	Alkaloids	473
	A Exocyclic Amines	473
	B Imidazole Alkaloids	475
	C Oxazole Alkaloids	475
	D Pyrrolidine and Pyrrolizidine Alkaloids	476
	Hygrine and Cuscohygrine 476, Senecio crotalaria Alkaloids 476	
	E Pyridine, Piperidine and Quinolizidine Alkaloids	479
	Tobacco Alkaloids 479, Alkaloids of <i>Lobelia syphilitica</i> 480, Alkaloids of <i>Sedum acre</i> L. 481, Securinega	

	Alkaloids 483, Erythrina Alkaloids 485, Nuphar Alkaloids 487, Lupine Alkaloids 489, Matrine and related Alkaloids 496, Lycopodium Alkaloids 498
F	Amaryllidaceous Alkaloids500 Lycorane Alkaloids 500, 5,10 b-Ethanophenanthridines 502, Acetal or Lactone Alkaloids 506, Dibenzofuran Derivatives 508
G	Quinazalone Alkaloids511
H	Tropane Alkaloids514
I	Quinoline Alkaloids514
J	Isoquinoline Alkaloids526 Tetrahydroalkylisoquinolines 527, Benzylisoquinolines and Tetrahydrobenzylisoquinolines 527, N-Bridged Tetrahydrodibenzocyclooctans 529, Aporphine Alkaloids 530, Tetrahydroberberine-type Tertiary Bases 543, Tetrahydroberberine methine-type Bases 547, Berberinium Bases 548, Protopine Alkaloids 550, Benzophenanthridine Alkaloids 550, Ipecac Alkaloids 554, Biscoclaurine Alkaloids 555, Morphinane Alkaloids 567
K	Indole Alkaloids573 Exocyclic Bases and Pyrrole Derivatives 575, Ergot Alkaloids 580, Yohimbe, Alstonia and Rauwolfia Alkaloids 590, Rutaceous Indole Alkaloids 613, Eserine and Related Alkaloids 616, Aspidosperma and Pleiocarpa Alkaloids 616, Geissospermum Alkaloids 638, Picralima Alkaloids 641, Vinca Alkaloids 645, Iboga Alkaloids 656, Strychnos and Curare Alkaloids 665
L	Steroid Alkaloids692 Holarrhena Alkaloids 692, Salamander Alkaloids 696, Buxus Alkaloids 698, Solanaceous Steroid Alkaloids 699, Veratrum Alkaloids 703
M	Diterpenoid Alkaloids712 Tuberostemonine 712, Atisine, Veatchine and Related Alkaloids 713, Songorine and Related Alkaloids 717, Hetisine and Related Alkaloids 717, Aconitine and Related Alkaloids 720
N	Miscellaneous Alkaloids, undetermined723 Colchicine and Related Alkaloids 723
O	Purine Derivatives725

1 Hydrocarbons and the Derivatives

[A] NMR Spectra

(1) Chemical shifts of protons are indicated in Table 1¹⁾

Table 1

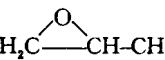
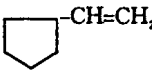
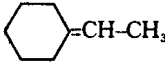
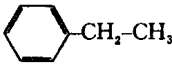
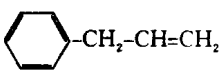
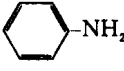
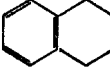
(Jungnickel *et al.*)¹⁾

Sample in 30% CCl₄ solv., sweep rate to 10 cps/s, δ =ppm to TMS (internal reference)

Compound	Proton of	Chem. shift δ
$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_2\text{C}=\text{CH}-\text{C}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	$=\text{CH}-$ $=\text{CH}_2$ $-\text{CH}_3$	5.75 4.83 1.00
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_3$	$=\text{CH}-$ $-\text{CH}_3, -\text{CH}_2-$	5.3 0.9~1.9
$\text{HC}\equiv\text{C}-\text{CH}_2-\text{CH}_3$	$\equiv\text{C}-\text{CH}_2-$ $\equiv\text{CH}$ $-\text{CH}_3$	2.17 1.78 1.14
$\begin{array}{c} \text{H}_2 \\ \\ \text{C} \\ / \quad \backslash \\ \text{H}_3\text{C} \quad \text{CH}_3 \end{array}$	$-\text{CH}_3$ ring- CH_2-	1.03 0.25
$\text{CH}_3-\text{CH}_2-\text{OH}$	$-\text{OH}$ $-\text{CH}_3$ $-\text{CH}_2-$	4.90 1.17 3.60
$\text{CH}_3-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$	$-\text{OH}$ $-\text{O}-\text{CH}_2-$ $-\text{CH}_3, -\text{CH}_2-$	4.7 3.5 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
$(\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-})_2\text{O}$	$\text{-CH}_2\text{-O-}$ $\beta\text{-CH}_2\text{-}$ $\text{CH}_3\text{-}$	3.30 1.50 0.90
$(\text{CH}_3\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-})_2\text{O}$	$\text{-CH}_2\text{-O-}$ $\text{CH}_3\text{-}, \text{-CH}_2\text{-}$	3.3 0.9~1.4
	$\text{-CH}_2\text{-O-CH-}$ -CH_3	2.2~2.8 1.22
$\text{CH}_3\text{-CH-CH}_2\text{-CH}_3$ SH	-S-CH $\text{-SH}, \text{-CH}_3, \text{-CH}_2\text{-}$	2.83 0.9~1.6
$\text{CH}_3\text{-S-CH}_2\text{-CH}_2\text{-CH}_3$	$\text{S-CH}_2\text{-}$ $\text{CH}_3\text{-S}, \text{-CH}_2\text{-CH}_3$	2.4 0.9~2.0
$\text{CH}_3\text{CH}_2\text{C(=O)CH}_3$	$\text{-CO-CH}_2\text{-}$ -CH_3	2.35 1.0
$\text{CH}_3(\text{CH}_2)_6\text{-C(=O)-O-(CH}_2)_3\text{-CH}_3$	$\text{-CO-O-CH}_2\text{-}$ $\text{CH}_3\text{-}, \text{-CH}_2\text{-}$	4.00 0.9~2.2
	$=\text{CH-}$ $\text{CH}_3\text{-}, \text{-CH}_2\text{-}$	5.20 1.7~2.2
	$=\text{CH-}$ $=\text{CH}_2$ $\text{-CH}_2\text{-}, >\text{CH-}$	5.66 4.83 1.5~2.4
	$=\text{CH-}$ $\text{CH}_3\text{-}, \text{-CH}_2\text{-}$	5.05 1.5~2.1
	Arom. H Ar. $\text{-CH}_2\text{-}$ -CH_3	7.05 2.53 1.15
	Arom. H $=\text{CH-}$ $=\text{CH}_2$	7.05 5.8 5.0
	Arom. H Ar. -NH_2	6.3~7.2 3.3
	Arom. H $\alpha\text{-CH}_2\text{-}$ $\beta\text{-CH}_2\text{-}$	6.85 2.60 1.66
	$\alpha\text{-CH}_2\text{-}$ $\beta\text{-CH}_2\text{-}, >\text{NH}$	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		CH ₃ -O-CO	6.2
C-NH ₂	8.4	CH ₃ -O-Ar	6.2
CH ₃ -C=C	8.2	H ₂ C=C	5.3
CH ₃ -C=O	8.0	H-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	7.2	CHO	0.2
		COOH	-0.8

(3) Typical coupling constants are indicated in Table 3

Table 3

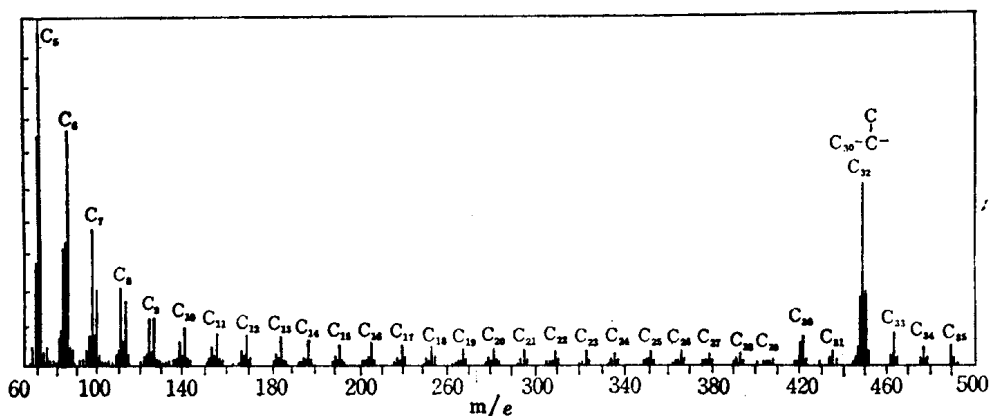
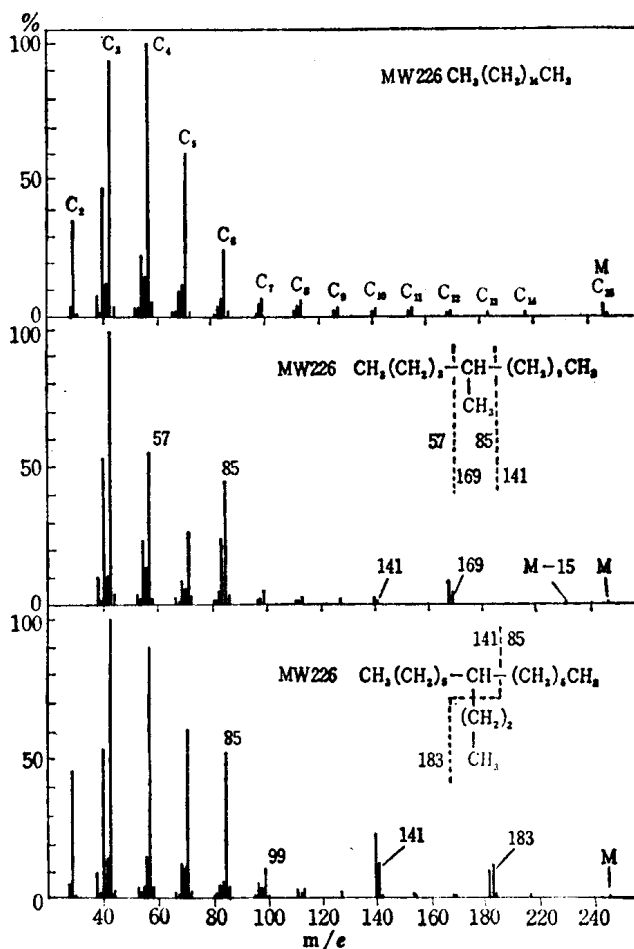
(Jones, R. A. Y *et al.*)

Group	J_{ab} (c/s)	Group	J_{ab} (c/s)
$\begin{array}{c} \text{H}_a \\ \diagup \\ \text{C} \\ \diagdown \\ \text{H}_b \end{array}$	12~15	$\begin{array}{c} \text{H}_a \diagup \text{C} = \text{C} \diagdown \text{H}_b \end{array}$	11~18
$\begin{array}{c} \text{H}_a \diagdown \text{C} - \text{C} \diagup \text{H}_b \end{array}$	8~12	$\begin{array}{c} \text{H}_a \diagup \text{C} = \text{C} \diagdown \text{H}_b \end{array}$	6~14
$\begin{array}{c} \text{H}_a \diagdown \text{C} - \text{C} \diagup \text{H}_b \end{array}$	2~4	$\begin{array}{c} \text{H}_a \diagup \text{C} = \text{C} \diagdown \text{CH}_b \end{array}$	0.5~2
Ha-C-C-C-Hb	0	$\begin{array}{c} \text{H}_a \diagup \text{C} = \text{C} \diagdown \text{CH}_b \end{array}$	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-Methyltetraatriacontane)^{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, docosanoic, tetra-
 cosanoic, 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 -spina-
 sterol from the heart wood of *Manikara bidentata*³⁾

[C] Naturally Occurring Polyene Compounds

(1) Hydrocarbons

(a) **Capillene** $\text{CH}_3\text{-C}\equiv\text{C-C}\equiv\text{C-CH}_2\text{-C}_6\text{H}_5$

(I)

<Occurrence> *Artemisia capillaris*⁴⁾, *A. dracunculus* L. and *Chrysanthemum frutescens* L.⁵⁾

UV λ_{max} $\text{m}\mu$ ($\log \epsilon$): 239, 253 (2.73, 2.63)⁴⁾

IR $\nu_{\text{max}} \text{cm}^{-1}$: 2270, 2210, 2160, 1960, 1600, 1500, 1380, 1075, 730, 695⁴⁾

(b) **Benzylodiacetylene** $\text{HC}\equiv\text{C-C}\equiv\text{C-CH}_2\text{-C}_6\text{H}_5$

(II)

<Occurrence> *Artemisia frutescens* L.⁵⁾ bp. 0.01 45~50°, n_D^{25} 1.5726

UV $\lambda_{\text{max}}^{\text{hexane}} \text{m}\mu(\epsilon)$: 267, 263.5, 257, 252, 247, 238.5, 226, 206.5, 196 (115, 184, 270, 400, 310,
 560, 660, 12000, 19000)⁵⁾

(c) **Aethusin** $\text{H}_3\text{C-CH=CH-(C}\equiv\text{C)}_2\text{-(CH=CH)}_2\text{-CH}_2\text{-CH}_3$

(III)

<Occurrence> *Aethusa cynapium* L.⁶⁾, mp. 23°, Colorless oil

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

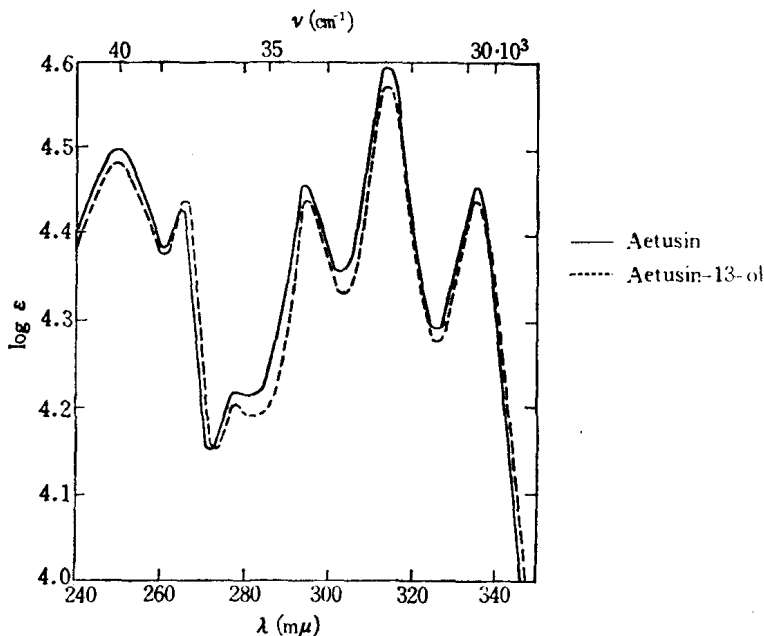


Fig. 3

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).

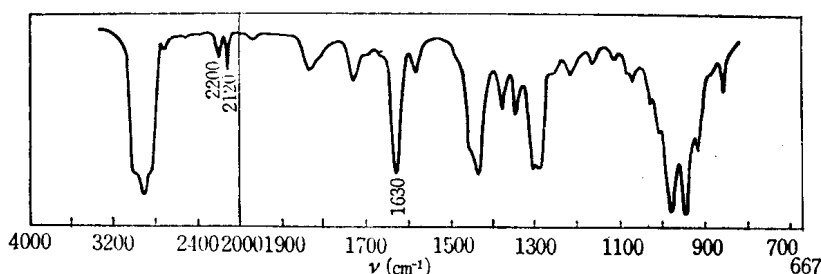


Fig. 4

- (d) **Tetraynediene**⁷⁾ $\text{H}_3\text{C}-\text{CH}=\text{CH}-(\text{C}\equiv\text{C})_4-\text{CH}=\text{CH}_2$ (IV)
 <Occurrence> *Centaurea cyanus* L. and other *Centaurea* spp., mp. 87°,
 UV $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$ μm : 389.5, 360.5, 336, 314.5, 287, 271, 258
 IR $\nu_{\text{max}}^{\text{CCl}_4} \text{cm}^{-1}$: 2190, 2120 ($-\text{C}\equiv\text{C}-$), 1650, 965, 925 ($-\text{CH}=\text{CH}_2$), 1615, 945 ($-\text{CH}=\text{CH}-$)
- (e) **Hydrocarbon**⁷⁾ $\text{H}_3\text{C}-\text{CH}=\text{CH}-(\text{C}\equiv\text{C})_2-(\text{CH}=\text{CH})_2-(\text{CH}_2)_4-\text{CH}=\text{CH}_2$ (V)
 <Occurrence> *Centaurea ruthenica* LAM.
 UV, IR.
- (f) **Centaur X₁**⁸⁾ $\text{H}_3\text{C}-\text{CH}=\text{CH}-(\text{C}\equiv\text{C})_2-(\text{CH}=\text{CH})_2-(\text{CH}_2)_4-\text{CH}=\text{CH}_2$ (VI)
 <Occurrence> *Centaurea ruthenica* L., (*trans* compound) mp. 28.5~29.5°
 UV $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$ $\mu\text{m}(\epsilon)$: 336, 314, 296, 279.5, 266, 250.5 (36300, 43400, 32050, 19650, 32800, 41000)
 IR $\nu_{\text{max}}^{\text{CCl}_4} \text{cm}^{-1}$: 1820, 1630, 912 ($-\text{CH}=\text{CH}_2$), 1625, 945 ($-\text{CH}=\text{CH}-$), 980 ($-(\text{CH}=\text{CH})_2-\text{trans}$), 2190, 2115 ($-\text{C}\equiv\text{C}-$)
- (g) **Tridecatriyne-(7,9,11)-triene-(1,3,5)**⁹⁾ (VII)
 $\text{H}_3\text{C}-(\text{C}\equiv\text{C})_3-\text{CH}=\text{CH}-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$
 <Occurrence> *Achillea ptarmica* and other *Achillea* spp.; *Anthemis* spp., mp. 88~93°
 UV $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$ μm : 356, 331, 311, 283
 IR $\nu_{\text{max}} \text{cm}^{-1}$: 2240 ($-\text{C}\equiv\text{C}-$), 1610, 1007 ($(\text{CH}=\text{CH})_2$), 1830, 910 ($-\text{CH}=\text{CH}_2$), 1385 ($(\equiv\text{C}-\text{CH}_3)$)

(2) Alcohols and their Acetates

- (a) **Centaur X₂**⁷⁾
 $\text{H}_3\text{C}-\text{CH}=\text{CH}-(\text{C}\equiv\text{C})_2-(\text{CH}=\text{CH})_2-\text{CH}_2-\underset{\text{OCOCH}_3}{\underset{\text{OCOCH}_3}{\text{CH}}}-(\text{CH}_2)_2-\text{OCOCH}_3$ (VIII)
 <Occurrence> *Centaurea macrocephala*, mp. 54~56°, $[\alpha]_D -5^\circ$ (MeOH)
 UV⁷⁾, IR $\nu_{\text{max}}^{\text{CHCl}_3} \text{cm}^{-1}$: 2190, 2125 ($-\text{C}\equiv\text{C}-$), 1615, 945 ($-\text{CH}=\text{CH}-$), 980 ($(\text{CH}=\text{CH})_2$), 1725, 1375, 1240 ($-\text{OAc}$)
 [Compounds] $\text{H}_3\text{C}-\text{CH}=\text{CH}-(\text{C}\equiv\text{C})_3-\text{CH}=\text{CH}-\underset{\text{R}_2}{\text{CH}}-\text{CH}_2-\text{OR}_1$ (IX)
- (b) **12, 13-Diacetoxytridecadiene (2,10)-triyne-(4,6,8)**^{7,8)} (IX) $\text{R}_1=\text{Ac}$, $\text{R}_2=\text{OAc}$
 <Occurrence> *Centaurea ruthenica* LAM., mp. 64⁹⁾, 76⁸⁾, $[\alpha]_D +102.2^\circ$ (CHCl_3)⁷⁾
 UV⁷⁾ $\lambda_{\text{max}}^{\text{Et}_2\text{O}}$ $\mu\text{m}(\epsilon)$ 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).