

occurred as doublets with the large coupling constants (8 Hz), a fact which indicated it to be a β -anomer. The rotation contribution of the glucose component in pteroside B ($[M]_D$ of pteroside B— $[M]_D$ of the aglycone (III) = -107) showed that the glucose involved is of the D series.³⁾

On the basis of the above evidence, pteroside B is concluded to be 2(R), 5,7-trimethyl-4-(2'-hydroxyethyl)-indan-1-one 2'- β -D-glucopyranoside (I).

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C-13 Resonance Chemical Shift for Substituted Ethyl and Isopropyl Derivatives

Recently, the C-13 resonance chemical shifts for organic compounds have become of interest from the physical, chemical, and biological view point.¹⁾ Numerous C-13 chemical shifts for liquid ethyl and isopropyl derivatives are presented in Tables I and II.

TABLE I. C-13 Chemical Shifts for C_2H_5R Derivatives Ref. CS_2 (ppm)

R	α -C	β -C	
NEt ₂	145.8	180.5	
NHEt	148.9	177.6	
OH	135.5	175.1	
OEt	127.4	178.3	
OCOMe	133.1	179.1	173.0 (OCO ¹³ Me)
Ph	163.8	177.3	
Cl	153.2	174.0	
Br	165.1	173.1	
CO ₂ H	165.6	184.6	
CO ₂ Me	166.1	184.4	142.3 (CO ₂ ¹³ Me)
CHO	156.0	187.1	
COMe	156.8	185.7	164.4 (CO ¹³ Me)
COEt	158.0	185.6	
CN	71.2	182.4	
NO ₂	122.4	181.6	
H ^{a)}	188.0	188.0	
Me ^{b)}	177.8	178.3	

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TABLE II. C-13 Chemical Shifts for Me₂CHR Derivatives Ref. CS₂ (ppm)

R	α -C	β -C	
OH	129.4	167.7	
OCOMe	125.3	170.8	171.6 (OCO ¹³ Me)
Et	161.4	171.4	163.3 (CH ₂) 181.9 (CH ₃)
Cl	133.1	165.7	
Br	148.2	164.1	
CO ₂ Me	159.3	174.4	142.2 (CO ₂ ¹³ Me)
CO ₂ H	159.1	174.7	
CN	173.2	173.2	69.3 (CN)
COMe	151.9	175.3	166.3 (CO ¹³ Me)
NO ₂	114.2	173.0	
H ^{a)}	177.8	178.3	
Me ^{b)}	169.1	169.1	

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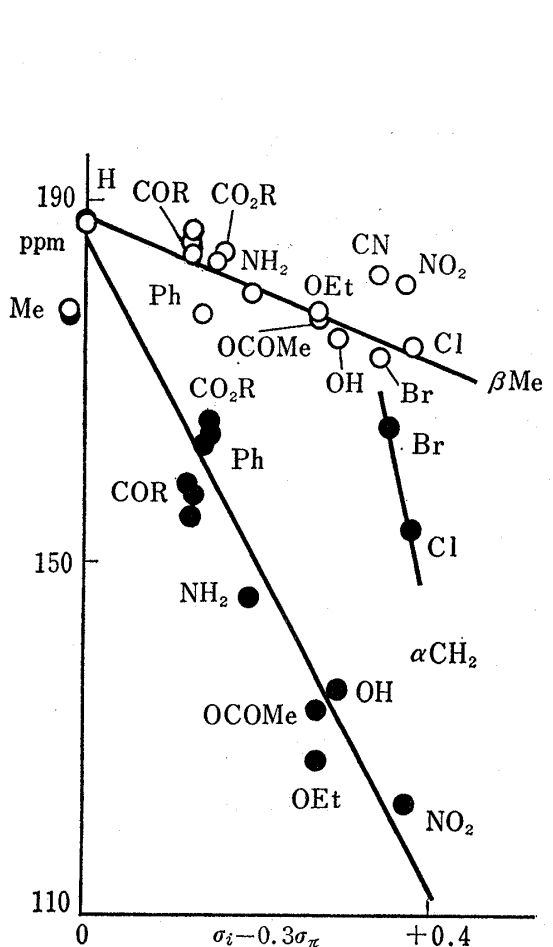


Fig. 1. C-13 Chemical Shifts for Substituted Ethyl Derivatives

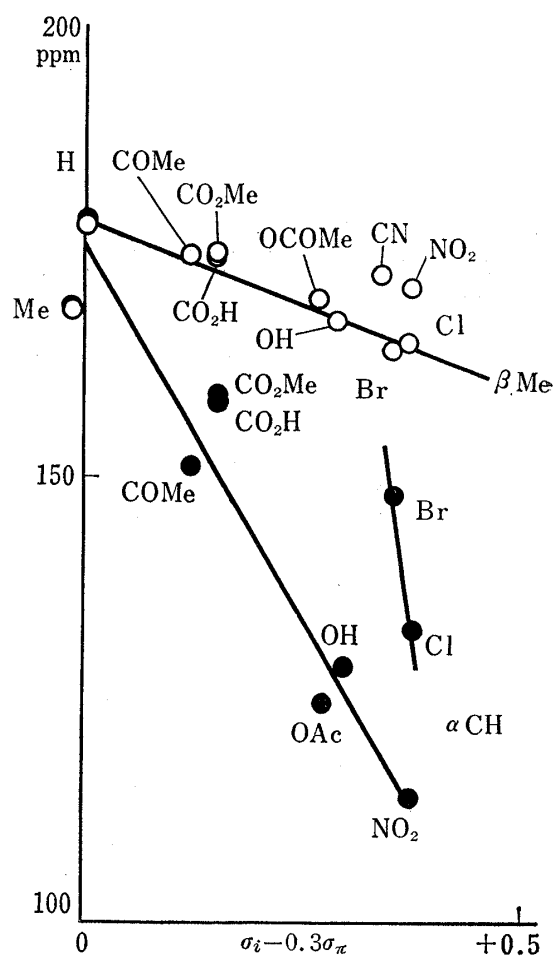


Fig. 2. C-13 Chemical Shifts for Substituted Isopropyl Derivatives

They were all determined by the normal and proton decoupling technique using Hitachi Perkin-Elmer Model R-20A spectrometer equipped with 15.085 MHz transmitter. These

shifts are arranged by the linear combination of the substituent constants σ_i and σ_π ,²⁾ and linear relations among both α - and β -C-13 chemical shifts with respect to $\sigma_i - 0.3 \sigma_\pi$ are observed as shown in Fig. 1 and 2.

Our previous study³⁾ confirmed that the α -H-1 chemical shifts for substituted methyl and ethyl derivatives are linear with $\sigma_i - 0.25 \sigma_\pi$, whereas those in the β - position, separated from the substituent group by three σ bonds, for ethyl and isopropyl derivatives are linear with σ_i , and from this fact it has been expected that the π -electronic effect, in other words, the delocalization effect, is effective through two σ bonds.

In the present, the same conclusion was verified for the β -C-13 resonance chemical shifts for substituted ethyl and isopropyl derivatives. Details of this work will be published in due time.

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Synthesis of 2-Thiouridine and 6-Methyl-3-(β -D-ribofuranosyl)-2-thiouracil

Recently several 2-thiopyrimidine nucleosides have been identified as the minor constituent of transfer ribonucleic acids (t-RNAs). 5-Methylaminomethyl-2-thiouridine and 2-thiocytidine were found in t-RNA of *E. coli*¹⁾ and 5-methoxycabonylmethyl-2-thiouridine was in t-RNA of baker's yeast.²⁾ 2-Thiocytidine has been prepared by the extended Hilbert-Johnson procedure from 4-amino-2-methylthiopyrimidine and a ribosyl chloride *via* the ribosyl pyrimidinium intermediate³⁾ and by the mercuri-procedure starting from diacetyl-2-thiocytosine.⁴⁾ Mercuric cyanide procedure⁵⁾ has recently been applied.⁶⁾ 2-Thiouridine, which had been prepared by the transformation of uridine through anhydronucleoside,⁷⁾ has been reported to be prepared by the mercuri-procedure starting from acetylated 2-thiouracil.⁴⁾ More recently, the silyl-procedure has been reported to be effective for 2-thiouridine synthesis.⁸⁾ These recent developments to the synthesis of 2-thiopyrimidine nucleosides prompted us to

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