ments showed the identity of these substances on the bases of the melting point, spectral data, and optical rotation. According to this result, the sites of the secondary hydroxyl group and three keto groups of digiprogenin were confirmed to agree with the presumed positions. The tertiary hydroxyl group was assumed to occupy the C-17 position in view of the conjugate system of anhydrodigiprogenin.

With respect to the conformation, the juncture of C/D rings is most likely to be *trans* in digipronin and γ-digiprogenin, and *cis* in isodigipronin and α-digiprogenin, on the basis of molecular rotations as follows :

$$\begin{array}{lcll} \text{digipronin } M_D & \longrightarrow & \text{isodigipronin } M_D & = \Delta M_D \\ -335.4^\circ & \longrightarrow & -376.0^\circ & = -40.6^\circ \end{array}$$

$$\begin{array}{lcll} \gamma\text{-digiprogenin } M_D & \longrightarrow & \alpha\text{-digiprogenin } M_D & = \Delta M_D \\ -261.0^\circ & \longrightarrow & -315.0^\circ & = -54.0^\circ \end{array}$$

Verification by chemical method is still to be made. Orientation of the 3-hydroxyl group was considered to be β, analogous to other natural steroids.

From these facts, it seems to be appropriate to assign (I), (II), (III), (IV) and (V) as the respective formulae for digipronin, isodigipronin, γ-digiprogenin, α-digiprogenin, and anhydrodigiprogenin.

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NMR Study of the Liquid Structure of Fatty Acids

The dilution shifts of the proton magnetic resonance in fatty acid-benzene and fatty acid-pyridine mixtures were measured. The fatty acids used in this experiment were acetic, dichloroacetic, propionic, butyric, isobutyric, and isovaleric acids.

Resonance of the Methyl Group

The observed shifts of the fatty acid-benzene mixture are shown in Fig. 1, where dichloroacetic acid (Curve A) and acetic acid (curve B) show larger shift than those of the others, for example, of isobutyric acid (curve C). Consistent with the result on chloroform-benzene mixture reported by Reeves and Schneider,[1] these high field shifts may be interpreted in terms of the π-complex formation between benzene and fatty acid molecule as illustrated in Fig. 2. By considering the values of these shifts, it is known that the strength of the bond between π-electron system and the methyl-hydrogen depends on chemical activity of the methyl group rather than on the molecular size and other steric effects.

In Fig. 3, the observed shifts of the fatty acid-pyridine mixtures are shown, where the active methyl, for example, that of acetic acid (curve A), shows shift to a low field more clearly than that of the less active methyl of butyric acid (curve B). This low field shift will suggest that the methyl-hydrogen locates in the plane of the pyridine ring, near the lone-pair electrons of the nitrogen as $-CH_3\cdots N$. Thus, it is clear from

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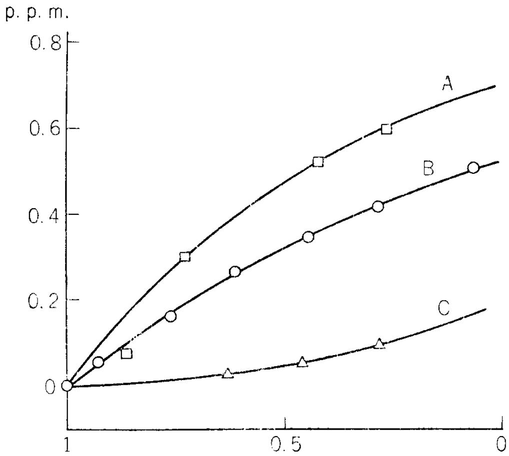
[1] L. W. Reeves, W. G. Scheider : Can. J. Chem., **35**, 251(1957).



Acid (molar fract.)
Fig. 1.
A: Dichloroacetic acid
B: Acetic acid
C: Isobutyric acid

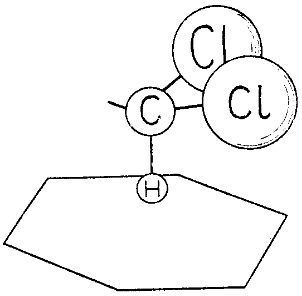


Fig. 2.

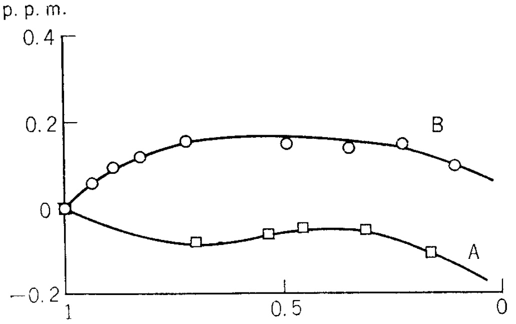


Fig. 3.
Acid (molar fract.)
A: Acetic acid
B: Butyric acid

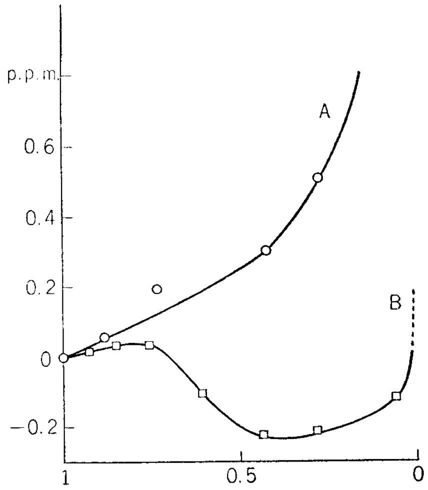


Fig. 4.
Acid (molar fract.)
A: Dichloroacetic acid
B: Acetic acid

this result that the active methyl behaves as a kind of weak acid in a basic solvent like pyridine.

Resonance of a Carboxylic Group

The results of measurements of fatty acid-benzene mixture are shown in Fig. 4, where zero point of the abscissa denotes the resonance position of pure acid. The behavior of dichloroacetic acid (curve A) is different from those of the others, for example, of acetic acid (curve B). The feature of curve B is almost consistent with the results for a mixture of acetic acid-aliphatic compound,²⁾ and may be interpreted by the degradation of liquid structures from the polymer to the monomer, via the dimer.²⁾ Contrary to curve B, curve A does not show the low field shift, which suggests that dichloroacetic acid does not form a dimer structure like other acids, and therefore, it is reasonable to consider that this acid has a long chain-like structure and is degradated gradually to the monomer without taking the (ring-like) dimer structure as diluted by

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benzene. The conclusion of this chain-like liquid structure for dichloroacetic acid seems to be capable of explaining the result obtained by the measurement of dielectric constant of this acid.³⁾

By examining detailed features of the curves, it is known that curve B has some resemblance to that of acetic acid-dichloroethane mixture,²⁾ i.e. acetic acid-aliphatic polar molecule mixture. This fact shows that benzene molecule is able to associate with the fatty acid molecules like aliphatic polar molecule.

More detailed discussions on the present matter will be reported elsewhere.

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February 2, 1960

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2) *Idem.* : Trans. Faraday Soc., **54**, 314(1958).
3) K. Nagano : Private communication.