those of the latter pair. The spectra also exhibit the ion peaks due to dehydration at m/e 486(in IIa) and m/e 500(in IIb) being coincided with the molecular ions of Ia and Ib. Especially of significance is that a fragment peak at m/e 302(c)[8] due to the reverse Diels-Alder type fragmentation in ring B of Ib is also observed in the mass spectrum of IIb, which suggests that a hydroxyl function in IIb locates at C-5 or C-6 and is readily dehydrated furnishing a double bond at C-5.

The C-6β-OH(axial) is preferred for IIa as based on the chemical property of IIa for acetylation and that of the derived carbonyl function in IId along with the proton magnetic resonance (PMR) assignment as given in Table I. A one-proton multiplet at 5.55 τ ($W_{h/2}=$ 8 Hz) of IIc is assignable to C-6α-H (equatorial).[9] Three C-methyl functions among six C-methyls (all observed as singlets) probably at C-4β, C-10β, and C-8β are observed paramagnetically shifted by suffering the anisotropic effect of C-6-OH, which is therefore considered to possess β-axial configuration.

Consequently, the structure IIa is proposed for protobassic acid. It is interestingly presumed that protobassic acid may be a genuine sapogenol of several *Sapotaceous* plants, in which bassic acid had been recognized as the common sapogenol. The structure of saponin is now under investigation.

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[8] Comfirmed by the high resolution mass spectrometry. Very recently, the ion(c) has also been described as a fragment ion of methyl sumaresinolate and its 6-oxo derivative by I. Wahlberg and C.R. Enzell (*Acta Chem. Scand.*, **25**, 70 (1971)).

[9] N.S. Bhacca and D.H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, 1964, p. 79.

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Thermal Hydrogen-Deuterium Exchange Reaction between Aromatic Ring Deuterium and Active Hydrogen of Substituent Group

With regard to the hydrogen-deuterium exchange reactions of organic compounds, numerous papers[1a–d] were presented. This communication is concerned to the thermal hydrogen-deuterium exchange observed in the substituted aromatics with active hydrogen atom on the substituent group. We prepared the deutrium labelled compounds by ordinary methods from

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[1] *a*) M. Eigen, *Angew. Chem.*, **75**, 489 (1963); *b*) J. Filip and Z. Koutecky, *Chem. Listy.*, **59**, 407 (1965); *c*) G.E. Calf, J.L. Garnett and W.A. Sollich-Baumgarten, *Advan. Tracer Methodolog.*, **4**, 11 (1968); *d*) W.T. Ford, W. Meister, R.D. Guthrie and J. Almy, *Am. Chem. Soc. Div. Petrol. Chem. Prepr.*, **13**, A29 (1968) And, the references cited therein.

C_6D_6, or from acid and base catalysed reaction of the substituted aromatics. The reaction course was followed up by the nuclear magnetic resonance (NMR) signal intensities. For example, when deuteroaniline, obtained by the catalytic hydrogenation of deuteronitrobenzene, is heated up to 150°, the ring H-1 NMR signal patterns of deuteroaniline (*ortho,* 4.5: *meta,* 2: *para,* 1) (*cf.* Fig. 1) are altered as shown in Fig. 2.

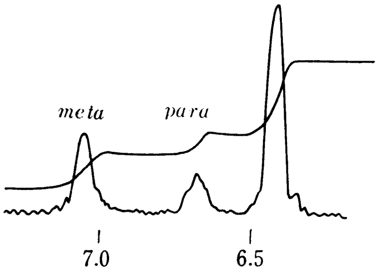

Fig. 1. Ring H-1 NMR Spectral Patterns of Deuteroaniline before Heating (TMS Reference)

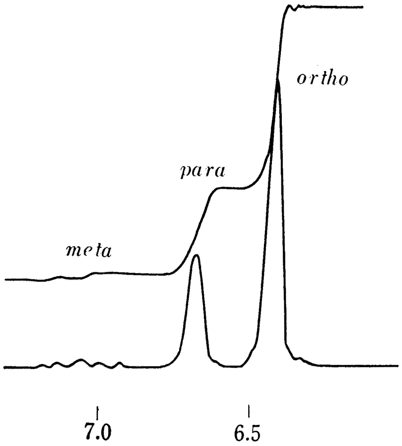

Fig. 2. Ring H-1 NMR Spectral Patterns of Deuteroanilne after Heating (TMS Reference)

This process, moreover, shows a time dependence and at an equilibrium after 50 minutes, the distributions of the H-1, averaged among NH_2, *ortho* and *para* positions, became 2: 2: 1 (*cf.* Fig. 3).

This result suggests that the mutual hydrogen-deuterium exchange between amino hydrogen and ring deuterium prefers *ortho* and *para* positions, respectively. Similar results are also observed in the substituted aromatics with substituent group containing active hydrogen (*e.g.* 4-substituted-2, 6-dideutero aniline and phenol series, *etc*), but not in N,N-dimethylaniline and anisole. The detail works will be published in the due time.

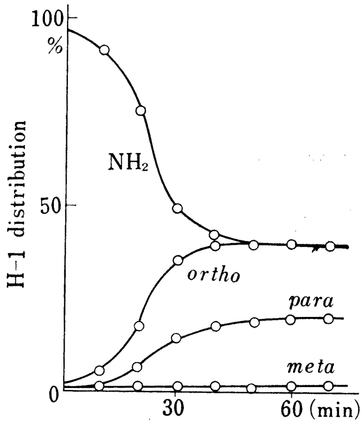

Fig. 3. The Time Dependence of H-1 Distribution of Deuteroaniline at 150°

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