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78. Tsutomu Momose, Yosuke Ohkura, and Shujiro Goya: Studies on Tetralin Derivatives. II.[1] Ultraviolet Spectra of Hydroxytetralins and Hydroxytetralones.

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Varying data on the ultraviolet spectra of tetralin and tetralone derivatives are to be found in the literatures. The absorption maxima of 1-hydroxy- and 2-hydroxytetralin,[2] tetralone,[3] 1-hydroxytetralone-(8), and 7-acetyl-1-hydroxytetralone-(8)[4] were measured in ethanol solutions, and absorption curves for tetralin in hexane,[5] 3-hydroxy- and 2-hydroxytetralone-(8),[6] 1,4,8-trihydroxytetralin-7-acetic acid lactone, and 8-hydroxy-1,4-diacetoxytetralin-7-acetic acid lactone in ethanol were shown.

The present paper gives the ultraviolet spectral data of 37 tetralin and tetralone derivatives, and describes the relations of the spectral properties to the substituted positions of hydroxyl, methoxyl, and acetoxyl groups attached to the aromatic ring of tetralin.

Materials 2,3-Diacetoxytetralin, 1,4-diacetoxytetralone-(8), and 2,3-diacetoxytetralone-(8) were obtained by the acetylation of the corresponding diphenols. Saponification of 1,4-diacetoxytetralone-(8) with 1 mole of sodium hydroxide gave an acetoxyhydroxytetralone. The position deacetylated is assumed to be 1, similar to the case of 1,4-dimethoxytetralone-(8)[1] from the fact that its oxime is precipitated by cupric, nickel, or ferric ion, forming a complex salt which is soluble in chloroform.

2,3-Dimethoxy-8-tetralone-7-acetic acid was prepared by the saponification of the condensation product of 2,3-dimethoxytetralone-(8) with ethyl bromoacetate. Demethylation of the acid gave 2,3-dihydroxy-8-tetralone-7-acetic acid. 2-Methoxy- and 2-hydroxy-8-tetralone-7-acetic acid were similarly synthesized by the condensation of 2-methoxytetralone-(8) with ethyl bromoacetate. Reduction of the hydroxy acid with sodium amalgam gave 2,8-dihydroxytetralin-7-acetic acid lactone, which was converted to the acetate by the usual method. 4,8-Dihydroxytetralin-7-acetic acid lactone was prepared by the diazotization of 4-amino-8-hydroxytetralin-7-acetic acid lactone, which was obtained by the reduction of the corresponding nitro compound. Acetylation of the dihydroxylactone gave 4-acetoxy-8-hydroxytetralin-7-acetic acid lactone. 1,3-Dihydroxy- and 1,3-diacetoxytetralin[6] were prepared in

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1) Part I. T. Momose, H. Oya, Y. Ohkura, M. Iwasaki: This Bulletin, **2**, 119(1954).
2) Komatsu, Masumoto, Kumamoto: Mem. Coll. Sci. Kyoto Imp. Univ., **7**, 287(1924).
3) H. Dannenberg, S. Läufer: Chem. Ber., **87**, 733(1954).
4) F. A. Hochstein, *et al.*: J. Am. Chem. Soc., **75**, 5455(1953).
5) R. A. Morton, A. J. A. De Gouveia: J. Chem. Soc., **1934**, 916.
6) K. Miki: J. Pharm. Soc. Japan, **61**, 272(1941).

accordance with references in the literatures.

The other tetralines and tetralones used had been prepared in earlier works.[1,7]

Spectra of Tetralins The ultraviolet absorption spectra of the substituted tetralins consist in general of two broad bands. These lie at 270 and $< 220\,m\mu$ in the case of tetralin. The hydroxyl group substituted in 2-position of tetralin has more bathochromic and hyperchromic effect than that in the 1-position, but the absorption maxima in the shorter wave length region of both hydroxytetralins still lie at $< 220\,m\mu$ (Fig. 1). The introduction of two hydroxyl groups in the aromatic

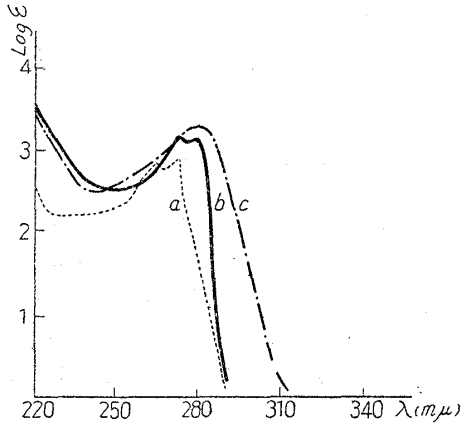

Fig. I. Ultraviolet Spectra of Teralin and *ar*-Hydroxytetralins (in EtOH)
a. Tetralin
b. 1-Hydroxytetralin
c. 2-Hydroxytetralin

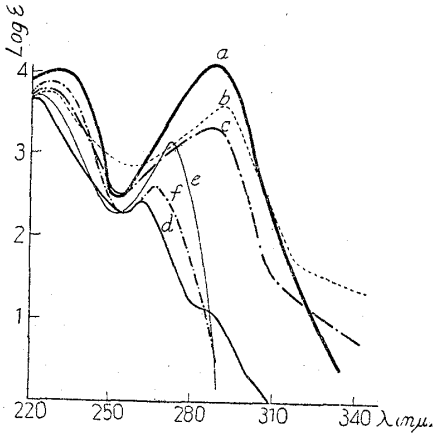

Fig. 2. Ultraviolet Spectra of *ar*-Dihydroxy- and *ar*-Diacetoxytetralins (in EtOH)
a. 1,4-Dihydroxytetralin
b. 2,3-Dihydroxytetralin
c. 1,3-Dihydroxytetralin
d. 1,4-Diacetoxytetralin
e. 2,3-Diacetoxytetralin
f. 1,3-Diacetoxytetralin

ring of tetralin causes a further increase of bathochromic effect. Thus, the second (shorter wave-length) band of 1,4-dihydroxytetralin lies at 233 $m\mu$, and those of 1,3- and 2,3-dihydroxytetralin lie at 227 $m\mu$ (Fig. 2). By the acetylation of the hydroxyl groups, the second band shifts to a shorter wave length region, except in the case of 1,3-dihydroxytetralin. The first band of three hydroxytetralins, which lies in the same region (287~291 $m\mu$), shows markedly hypochromic and hypsochromic shift by the acetylation.

The introduction of a hydroxy-lactone ring in the hydroaromatic ring of tetralin

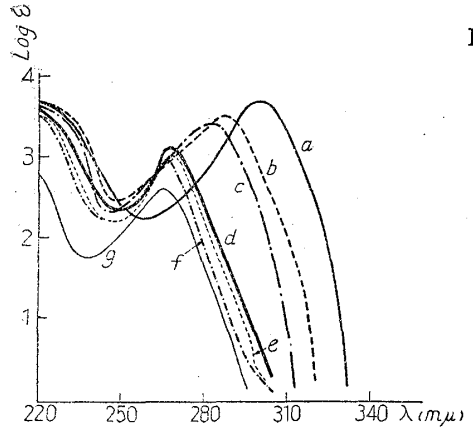

Fig. 3. Ultraviolet Spectra of Hydroxytetarlin-7-acetic Acid Lactones (in EtOH)
a. 1,4,8-Trihydroxytetralin-7-acetic acid lactone
b. 2,8-Dihydroxytetralin-7-acetic acid lactone
c. 4,8-Dihydroxytetralin-7-acetic acid lactone
d. 8-Hydroxy-1,4-diacetoxytetralin-7-acetic acid lactone
e. 8-Hydroxy-2-acetoxytetralin-7-acetic acid lactone
f. 8-Hydroxy-4-acetoxytetralin-7-acetic acid lactone
g. 8-Hydroxytetralin-7-acetic acid lactone

7) Y. Asahina, T. Momose : J. Pharm. Soc. Japan, **64**, 153(1944).

gives only a small influence on the spectra. The absorption curve of 8-hydroxytetralin-7-acetic acid lactone resembles that of tetralin in general form and intensity, and the substitution of one or two hydroxyl groups causes a hyperchromic and bathochromic shift, which returns to the original by the acetylation (Fig. 3).

The wave lengths and the molecular extinction coefficients at the absorption maximum of the above hydroxytetralins are listed in Table I.

Table I. Ultraviolet Absorption Maxima of Tetralin and Hydroxytetralin Derivatives (in EtOH)

Compound	λ_{max} (mμ)	log ε	λ_{max} (mμ)	log ε
Tetralin			266.5	2.85
			274	2.91
1-OH-tetralin			273	3.18
			280	3.13
2-OH-tetralin			283	3.32
1,4-diOH-tetralin	233	4.01	288	4.07
1,3-diOH-tetralin	227	3.81	287	3.37
2,3-diOH-tetralin	227	3.75	291	3.60
1,4-diAcO-tetralin	221	3.69	262.5	2.46
1,3-diAcO-tetralin	227	3.97	265	2.66
2,3-diAcO-tetralin	222	3.75	272	3.18
2,3-diCH_3O-tetralin	230	3.79	287	3.57
8-OH-tetralin-7-acetic acid lactone			265	2.56
2-OH-tetralin-7-acetic acid lactone			287	3.50
4-OH-tetralin-7-acetic acid lactone			284	3.41
2-AcO-tetralin-7-acetic acid lactone			270	3.02
4-AcO-tetralin-7-acetic acid lactone			261	2.91
1,4-diOH-tetralin-7-acetic acid lactone			300	3.71
1,4-diAcO-tetralin-7-acetic acid lactoue			265	3.06

Spectra of Tetralones The subsituted tetralones have in general three absorption bands. In the case of tetralone, two bands are observed at 293 and 248 mμ, and the third band may be in a far shorter wave length region which cannot be measured. The introduction of a hydroxyl group in 1-, 4-, or 2-position of tetralone causes a strong bathochromic effect in the first (longest wave-length) band, but only a small effect in the second band. On the contrary, the introduction of a hydroxyl group in 3-position shows a stronger effect in the second band, so that the first appears only as a shoulder on the longer wave side of the second (Fig. 4). The third band is observed at 228 mμ in 3-hydroxy- and 2-methoxytetralone-(8).

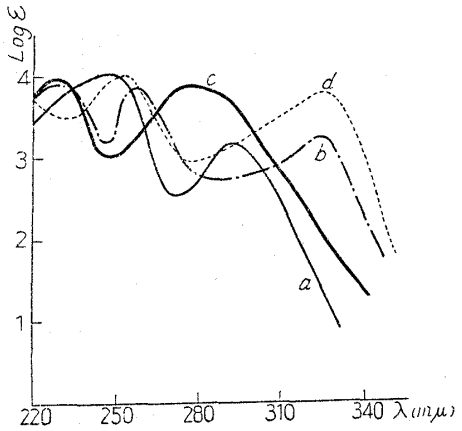

Fig. 4. Ultraviolet Spectra of Tetralone and *ar*-Hydroxytetralones (in EtOH)

a. Tetralone
b. 4-Hydroxytetralone
c. 3-Hydroxytetralone
d. 2-Hydroxytetralone

Dihydroxytetralones have also three bands. The first band appears at > 293 mμ, the second at 252~282 mμ, and the third in a region below 240 mμ. The introduction of two hydroxyl groups in 1- and 4-positions of the aromatic ring causes a more bathochromic shift in the first band than that of 2,3-positions, moving the

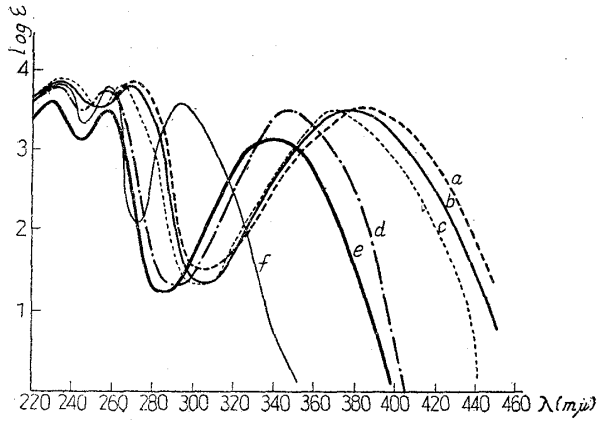

Fig. 5. Ultraviolet Spectra of 2-Methyl-1,4-dihydroxytetralone-(8), 1,4-Dihydroxytetralone-(8) and their Acetates and Methyl Ethers (in EtOH)

a. 2-Methyl-1,4-dihydroxytetralone-(8)
b. 1,4-Dihydroxytetralone-(8)
c. 1-Hydroxy-4-methoxytetralone-(8)
d. 1,4-Dimethoxytetralone-(8)
e. 1-Hydroxy-4-acetoxytetralone-(8)
f. 1,4-Diacetoxytetralone-(8)

absorption maximum to a nearly visible region (Fig. 5). Thus, the crystals of 1,4- and 2-methyl-1,4-dihydroxytetralone-(8) have yellow and orange colors, respectively. In the second band, the hydroxyl groups substituted in 2,3-positions show a more bathochromic effect than that of 1,4-positions, corresponding to the fact that 3-hydroxytetralone-(8) has the strongest effect on the second band as described above (Fig. 6). By acetylation or methylation of the diphenols, an increasing hypsochromic

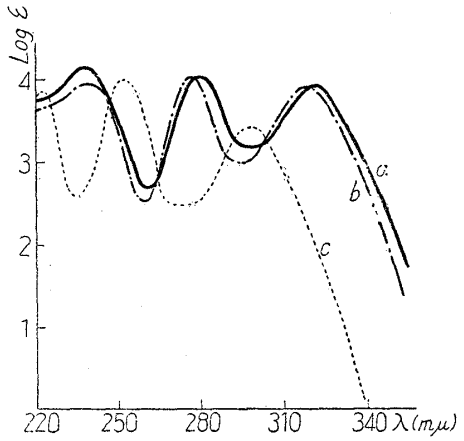

Fig. 6. Ultraviolet Spectra of 2,3-Dihydroxytetralone-(8), its Dimethyl Ether, and Diacetate (in EtOH)

a. 2,3-Dihydroxytetralone-(8)
b. 2,3-Dimethoxytetralone-(8)
c. 2,3-Diacetoxytetralone-(8)

shift is observed in the order of diacetoxy>acetoxy-hydroxy>dimethoxy>methoxy-hydroxy on the first and the second bands in the 1,4-disubstituted tetralones, and also on the third band in 2,3-diacetoxytetralone-(8).

2-Hydroxy-8-tetralone-7-acetic acid has an absorption curve which is similar in shape to that of 2-hydroxytetralone-(8), except that the first band is less intense than that of the tetralone. The absorption curve of the methyl ether of the acid resembles that of 2-methoxytetralone-(8). Therefore, the introduction of acetic acid in 7-position of tetralone has only a small effect on the spectra, and the absorption

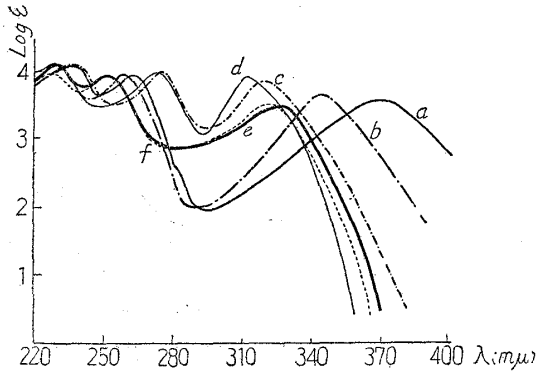

Fig. 7. Ultraviolet Spectra of Hydroxy-8-tetralone-7-acetic Acids (in EtOH)

a. 1,4-Dihydroxy-8-tetralone-7-acetic acid
b. 1,4-Dimethoxy-8-tetralone-7-acetic acid
c. 2,3-Dihydroxy-8-tetralone-7-acetic acid
d. 2,3-Dimethoxy-8-tetralone-7-acetic acid
e. 2-Hydroxy-8-tetralone-7-acetic acid
f. 2-Methoxy-8-tetralone-7-acetic acid

curves of dihydroxy-8-tetralone-7-acetic acids and their methyl ethers are similar in shape to that of the corresponding dihydroxytetralones and their methyl ethers (Fig. 7).

The wave lengths and the molecular extinction coefficients at the absorption maximum of the above tetralones are summarized in Table II.

Table II. Ultraviolet Absorption Maxima of Tetralone and Hydroxytetralone Derivatives (in EtOH)

Compound	λ_{max}(mμ)	log ε	λ_{max}(mμ)	log ε	λ_{max}(mμ)	log ε
Tetralone			248	4.08	293	3.25
1-OH-tetralone*			260	3.95	335	3.52
2-OH-tetralone			253	4.05	325	3.80
3-OH-tetralone	228	4.01	272.5	3.95		
4-OH-tetralone	228	3.92	258	3.86	323	3.35
1-OH-7-Ac-tetralone*			267	3.74	348	4.09
2-CH_3O-tetralone	228	3.93	252	3.95	318	3.49
2-CH_3-1,4-diOH-tetralone	233	3.90	270	3.88	381	3.56
1,4-diOH-tetralone	232	3.88	268	3.82	372	3.54
1-OH-4-CH_3O-tetralone	233	3.87	263	3.80	368	3.52
1,4-diCH_3O-tetralone	233	3.87	260	3.75	343	3.55
1-OH-4-AcO-tetralone	231	3.61	259	3.55	339	3.19
1,4-diAcO-tetralone	232	3.85	258	3.80	293	3.56
2,3-diOH-tetralone	237	4.17	278	4.08	321	3.97
2,3-diCH_3O-tetralone	240	3.98	276	4.08	316	3.88
2,3-diAcO-tetralone	221	3.87	252	4.02	295	3.43
8-Tetralone-2-acetic acid						
2-OH-tetralone-2-acetic acid	228	4.10	250	3.96	325	3.53
2-CH_3O-tetralone-2-acetic acid	230	3.96	250	3.96	319	3.55
1,4-diOH-tetralone-2-acetic acid	238	4.08	262	3.92	370	3.64
1,4-diCH_3O-tetralone-2-acetic acid	230	4.05	248	3.98	342	3.66
2,3-diOH-tetralone-2-acetic acid	236	4.10	274	3.99	317	3.87
2,3-diCH_3O-tetralone-2-acetic acid	232	4.08	275	4.07	310	3.92

* These data are cited from the literature in Footnote (4).

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Experimental

2,3-Diacetoxytetralin—2,3-Dihydroxytetralin was acetylated with Ac_2O and 1 drop of H_2SO_4. After decomposing the anhydride with water, the separated crystals were recrystallized from EtOH to plates of m.p. 115~116°. *Anal.* Calcd. for $C_{14}H_{16}O_4$: C, 67.73; H, 6.50. Found: C, 67.44; H, 6.83.

1,4-Diacetoxytetralone-(8)—1,4-Dihydroxytetralone-(8) was acetylated with Ac_2O and H_2SO_4, and recrystallized from AcOEt to needles of m.p. 175°. *Anal.* Calcd. for $C_{14}H_{14}O_5$: C, 64.11; H, 5.38. Found: C, 63.84; H, 5.51.

2,3-Diacetoxytetralone-(8)—2,3-Dihydroxytetralone-(8) was acetylated with Ac_2O and H_2SO_4, and recrystallized from AcOEt to prisms, m.p. 136°. *Anal.* Calcd. for $C_{14}H_{14}O_5$: C, 64.11; H, 5,38. Found: C, 63.95; H, 5.32.

1-Hydroxy-4-acetoxytetralone-(8)—3 g. of well powdered 1,4-diacetoxytetralone-(8) was added to a solution of 0.5 g. of NaOH in 25 cc. of water, and refluxed for 10 mins. The mixture was acidified with dil. HCl, after cooling and the separated crystals were recrystallized from benzene-EtOAc (9 : 1) to colorless needles of m.p. 136°. Yield 1.5 g. *Anal.* Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.32; H, 5.30.

The oxime was prepared in dil. EtOH with H_2NOH-HCl and AcONa, and recrystallized from dil. EtOH to plates of m.p. 119°. *Anal.* Calcd. for $C_{12}H_{13}O_4N$: N, 5.96. Found: N, 6.12.

2,3-Dimethoxy-8-tetralone-7-acetic Acid—2.3 g. of $NaNH_2$ was added to a solution of 10 g. of 2,3-dimethoxytetralone-(8) in 200 cc. of anhyd. benzene, and refluxed for 6 hrs. in an atmosphere of H_2. The resulting mixture was cooled in an ice bath, and a solution of 10 g. of ethyl bromoacetate in 20 cc. of anhyd. benzene was added gradually. The mixture was refluxed an additional 3 hrs., decomposed with dil. HCl, and the separated benzene layer evaporated. The resinous residue was refluxed 2 hrs. with 200 cc. of 10% aq. NaOH. The alkaline solution was washed with benzene,

acidified with dil. HCl, and extracted repeatedly with benzene. After removal of benzene a small amount of MeOH was added to the residue, and the separated crystals (2 g.) were recrystallized from MeOH to prisms of m.p. 182°. *Anal.* Calcd. for $C_{14}H_{16}O_5$: C, 63.62; H, 6.10. Found: C, 63.63; H, 6.06.

2,3-Dihydroxy-8-tetralone-7-acetic Acid—1.5 g. of the above dimethyl ether was refluxed with 5 g. of 50% HI for 15 mins. in an atmosphere of CO_2, then 30 cc. of water was added. The separated crystals were recrystallized from water to prisms of m.p. 240°. *Anal.* Calcd. for $C_{12}H_{12}O_5$: C, 61.01; H. 5.12. Found: C, 60.83; H, 5.05.

2-Methoxy-8-tetralone-7-acetic Acid—Prepared similarly by the condensation of 2-methoxytetralone-(8) with ethyl bromoacetate. It was recrystallized from EtOH to prisms of m.p. 126°. *Anal.* Calcd. for $C_{13}H_{14}O_4$: C, 66.65; H, 6.02. Found: C, 66.49; H, 5.55.

2-Hydroxy-8-tetralone-7-acetic Acid—Obtained by the demethylation of the ether by HI. It was recrystallized from EtOH to prisms of m.p. 188~189°. *Anal.* Calcd. for $C_{12}H_{12}O_4$: C, 65.44; H, 5.49. Found: C, 65.62; H, 5.20.

2,8-Dihydroxytetralin-7-acetic Acid Lactone. To a solution of 1.5 g. of the above tetralone in 50 cc. of 2% aqueous solution of $NaHCO_3$, 20 g. of 3% sodium amalgam was added, and stirred 12 hrs. in an atmosphere of CO_2. The aqueous layer was acidified with dil. HCl, and the separated crystals were recrystallized from EtOH to prisms of m.p. 142°. *Anal.* Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.14; H, 5.80.

2-Acetoxy-8-hydroxytetralin-7-acetic Acid Lactone—Obtained by the acetylation of the above phenol with Ac_2O and H_2SO_4. Recrystallization from EtOH gave prisms of m.p. 98°. *Anal.* Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.16; H, 6.06.

4-Amino-8-hydroxytetralin-7-acetic Acid Lactone—To a solution of 2 g. of 4-nitro-8-hydroxytetralin-7-acetic acid lactone[8] and 0.5 g. of NH_4Cl in 50 cc. of 50% EtOH, 2 g. of zinc dust was added, and refluxed for 2 hrs. The hot mixture was filtered from zinc, diluted with water, and allowed to stand overnight. The separated crystals (1 g.) were recrystallized from benzene to prisms of m.p. 155°. *Anal.* Calcd. for $C_{12}H_{13}O_2N$: C, 70.91; H, 6.45. Found: C, 70.48; H, 6.39.

4,8-Dihydroxytetralin-7-acetic Acid Lactone—A solution of 0.8 g. of the above amine in 50 cc. of 5% HCl was cooled in an ice bath to about 10°, and diazotized with a solution of 0.3 g. of $NaNO_2$ in 10 cc. of water. The mixture was warmed 10 mins. in a water bath at about 60°, and after cooling, the separated crystals were recrystallized from EtOH to prisms of m.p. 176~177°. *Anal.* Calcd. for $C_{12}H_{12}O_3$: C, 70.57; H, 5.92. Found: C, 70.39; H, 5.81.

4-Acetoxy-8-hydroxytetralin-7-acetic Acid Lactone—Obtained by the acetylation of the phenol. It was recrystallized from EtOH to prisms of m.p. 125°. *Anal.* Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.37; H, 5.88.

Ultraviolet absorption spectra—The spectra were determined by a Shimadzu Photoelectric Spectrophotometer type QB-50 with a quartz cell of 10 mm. optical depth in the wave length region of 220~400 mμ at 13°±3°. The materials were dissolved in purified EtOH at varying concentrations from 3×10^{-3} to $1\times10^{-4}M$.

Summary

The ultraviolet absorption spectra of hydroxytetralins, hydroxytetralones, their acetates, and their methyl ethers are compared. The spectra of hydroxytetralin derivatives consist of two bands, and that of hydroxytetralone derivatives, three bands. The introduction of a hydroxyl group to the aromatic ring of tetralin displaces the absorption band to a longer wave length region, increasing the intensity. The introduction of two hydroxyl groups, especially in 1,4-positions, is more effective. The acetylation and the methylation of the hydroxyl group decrease the spectral effect of hydroxyl group in varying rates. Syntheses of some tetralin and tetralone derivatives are also described.

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