Summary

A fluorescent compound produced in the reaction of 5-hydroxy-1-tetralone with glucose in sulfuric acid was separated in crystalline form and its probable structure was forwarded as benzonaphthenedione. The same compound was also isolated from the reaction mixture of glyceraldehyde with the same reagent. The mechanism of these reactions was discussed.

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80. Tsutomu Momose, Yo Ueda, and Tatsuo Shōji : Organic Analysis. XI.*

Infrared Spectra of Phenylsulfonyl Derivatives. (1).

The SO₂ Stretching Frequencies.

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Several infrared spectral studies on phenylsulfonyl derivatives were reported by Schreiber,¹⁾ Amstutz, *et al.*,²⁾ and by Barnard, *et al.*³⁾ concerning mainly with the hydrogen-bond formation of sulfonyl group. Bellamy,⁴⁾ quoting the data of Haszeldine,⁵⁾ Barnard,³⁾ and Baxter,⁶⁾ and their co-workers, concluded that the substituent effect of a sulfonyl group was much smaller than that of a carbonyl group, because sulfonyl group has a tetrahedral structure.

However, since sulfonyl group has decet electronic structure in its resonance state

of $\begin{array}{c} \text{O} \\ \parallel \\ -\text{S}- \\ \mid \\ \text{O} \end{array} \longleftrightarrow \begin{array}{c} \text{O} \\ \mid \\ -\text{S}- \\ \parallel \\ \text{O} \end{array}$, and has a double bond-like character, some substituent effect of

this group may be expected. Thus, Amstutz, *et al.* already found a shift of 3 cm⁻¹ between 4-hydroxydiphenyl and 4-hydroxy-2-methoxydiphenyl sulfones, and Vogl-Högler⁷⁾ recognized some constitutive influence upon the SO frequencies. Szmant, *et al.*⁸⁾ assumed from the study of ultraviolet spectra that when a phenylsulfonyl compound had an

electron-accepting radical it might take a structure of $\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{S}-\text{R}' \\ \mid \\ \text{O} \end{array}$, and when it had an

electron-donating radical it might take a structure of $\begin{array}{c} \text{O}^- \\ \parallel \\ \text{R}-\text{S}^+-\text{R}' \\ \mid \\ \text{O}^- \end{array}$.

In this paper, infrared spectra of 50 phenylsulfonyl derivatives that were measured and substituent effect on the sulfonyl group are discussed.

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1) K.C. Schreiber : Anal. Chem., **21**, 1168(1949).

2) E.D. Amstutz, I.M. Hunsberger, J.J. Chessick : J. Am. Chem. Soc., **73**, 1220(1951).

3) D. Barnard, J.M. Fabian, H.P. Koch : J. Chem. Soc., **1949**, 2442.

4) L.J. Bellamy, R.L. Williams : *Ibid.*, **1957**, 863.

5) R.N. Haszeldine, J.M. Kidd : *Ibid.*, **1955**, 2901.

6) J.N. Baxter, J. Cymerman-Craig, J.B. Willis : *Ibid.*, **1955**, 669.

7) R. Vogl-Högler : Acta Phys. Austriaca, **1**, 323(1948) (C.A., **42**, 6663(1948)).

8) H.H. Szmant, G. Suld : J. Am. Chem. Soc., **78**, 3400(1956); H.H. Szmant, J. Dixon : *Ibid.*, **78**, 4384(1956).

Results and Discussion

Nature of the Spectra

Most of phenylsulfonyl derivatives were sparingly soluble in organic solvents except alcohols, and a Nujol mull method was used for all the samples. However, several typical compounds on which main discussion is based were measured in CHCl_3 solution to avoid any molecular aggregation effect. All compounds showed very strong bands of an asymmetric (ν_{as}) and a symmetric (ν_{s}) stretching mode of an S-O bond.

Fig. 1 shows typical spectra, and also the difference of vibration frequencies measured in Nujol mull (—) and in CHCl_3 solution (-----). The ν_{as} frequencies in the solution spectra have $10\sim 20\text{ cm}^{-1}$ higher values than that of the solid spectra, but the ν_{s} frequencies do not show such large differences and conversely have rather diminishing tendencies. This result agrees with that of the studies of Barnard and Baxter. By the explanation of Barnard, the asymmetric vibration frequency is of a more purely bond-stretching type than the symmetric frequency, and the former may undergo a much greater shift.

Fig. 1.
Infrared Spectra of Phenylsulfonyl
Derivatives

— Nujol mull
----- CHCl_3 solution

1. Phenylsulfonylmethane
2. 4-Methylphenylsulfonylmethane
3. 4-Aminophenylsulfonylmethane
4. 4-Cyanophenylsulfonylmethane

Fig. 1 also shows that the solid spectra has a characteristic feature; namely, their absorption bands are more broad and complex than that of the solution spectra. Therefore, when these bands overlap other bands, some difficulties may occur in the assignment of the group, and then a solution method will be recommended.

The SO_2 frequencies measured are listed in Tables I and II. The ν_{s} appears as one maximum absorption band or accompanied with one shoulder, and the ν_{as} appears as two absorption bands or accompanied with one shoulder. In the solid spectra, most of the ν_{as} consist of a few frequencies, but they have, in general, one maximum frequency which corresponds to the main band of the solution spectra. Then this maximum frequency becomes important in the discussion, and is listed in bold-face type in

Fig. 2. Frequency Shifts of *para*-Substituted Phenylsulfonyl-methanes

the table. The ν_{as} has a range of $1339\sim1279\text{ cm}^{-1}$ ($7.47\sim7.82\mu$) in the solid state and of $1326\sim1305\text{ cm}^{-1}$ ($7.54\sim7.66\mu$) in the solution. The ν_s has a range of $1172\sim1136\text{ cm}^{-1}$ ($8.53\sim8.80\mu$) in the solid state, and of $1157\sim1144\text{ cm}^{-1}$ ($8.64\sim8.74\mu$) in the solution.

Substituent Effect

At first, phenylsulfonylmethane and *p*-amino-, *p*-hydroxy-, *p*-methyl-, and *p*-cyano-phenylsulfonylmethane were compared with each other. Fig. 2 shows that when phenylsulfonylmethane is taken as a standard *p*-NH₂ has the greatest shift of the ν_{as} to a longer wave-length region, and *p*-CN shows a shift to a shorter wave-length region, whereas there is no such great shift of the ν_s in any of the compound.

The order of the shift of ν_{as} coincides with the order of Hammett's σ^9 (*p*-NH₂ : -0.660 , *p*-OH : -0.357 , *p*-CH₃ : -0.170 , *p*-CN : $+0.628$) and with that of the chemical shift of benzene derivatives¹⁰⁾ (*p*-NH₂ : -0.40 , *p*-OH : -0.37 , *p*-CH₃ : -0.10 , *p*-CN : $+0.30$). It may be supposed that if the electron density of S atom diminishes, a double bond character of S-O will increase, and then the force constant of the bond will become larger, absorbing in a shorter wave length region, and vice versa. *p*-Amino-phenylsulfonylmethane can be written in resonance forms (Ia $\longleftrightarrow$ Ib).

TABLE I. Infrared Absorption Bands of SO₂ Group in Phenylsulfonylmethane Derivatives

Compd. No.	R ₃	R ₂	State	$\nu_{as}^{a)}$		$\epsilon_{\max}$	$\nu_s^{a)}$	$\epsilon_{\max}$	Mean freq.
(I)	H		N	1297 ^{b)}	1285		1143		1214
(I)	H		C	1321	1314	556	1152	932	1237
(II)	CH ₃		N	1304	1287		1149		1227
(II)	CH ₃		C	1318	1302	774	1149	1187	1234
(III)	NH ₂		N	1282			1140		1211
(III)	NH ₂		C	1305		674	1144	1319	1225
(IV)	OH		N	1282 ^{c)}			1144 ^{c)}		1213
(IV)	OH		C	1307		481	1144	1094	1226
(V)	CN		N	1319	1290		1156		1238
(V)	CN		C	1326			1152		1239
(VI)	CH ₃ CONH		N	1284	1263		1138		1211
(VII)	(CH ₃ CO) ₂ N		N	1300	1282		1148		1224
(VIII)	HCl·H ₂ NCH ₂		N	1314	1304 ^{b)}	1292	1155		1235
(IX)	HCl·H ₂ NCH ₂	Cl	N	1311			1149		1230
(X)	HCl·H ₂ N(CH ₃)CH		N	1309	1289		1151		1230
(XI)	HCONHCH ₂ ¹¹⁾		N	1314	1297		1144		1221
(XII)	CH ₃ CONHCH ₂ ¹²⁾		N	1316	1297	1285	1152		1225
(XIII)	(CH ₃ CO) ₂ NCH ₂		N	1304	1287	1267	1147		1226
(XIV)	P ¹¹⁾		N	1307	1292 ^{b)}		1142		1225
(XV)	CHO	Cl	N	1311	1290		1157		1234

9) H. H. Jaffé : Chem. Revs., **53**, 191(1953).

10) B. P. Dailey, et al. : J. Am. Chem. Soc., **78**, 3043(1956).

11) T. Momose, T. Shōji : Yakugaku Zasshi, **70**, 616(1950).

12) K. A. Jensen, et al. : Z. Physiol. Chem., **280**, 35(1944).

(XVI)	(CH ₃ CO ₂) ₂ CH		N	1309	1292	1160	1235
(XVI)	(CH ₃ CO ₂) ₂ CH		C	1323		1153	1238
(XVII)	(CH ₃ CO ₂) ₂ CH	Cl	N	1321		1153	1237
(XVIII)	HON=CH ¹¹⁾		N	1307	1289	1153	1230
(XIX)	HON=CH	Cl	N	1302	1294	1147	1225

a) Maximum absorption in bold-face type. b) Shoulder. c) Broad.

N: Nujol. C: CHCl₃ solution. P: Phthaliminomethyl.

The structure (Ib) may be possible by the +M effect of NH₂, and the S-O bond may have greater single-bond character than phenylsulfonylmethane, absorbing at a fairly longer wave-length region. The +M effect of *p*-OH is next to that of *p*-NH₂ and the shift is also in the following step. *p*-CH₃ has a +I effect, and absorbs at a somewhat longer wave-length region. The effect of *p*-OH cannot be directly compared with that of *p*-CH₃, but in general it is known that *p*-OH has a greater influence than *p*-CH₃, and the results shown in Fig. 2 agree with this order. *p*-CN has -I effect and will give a greater double-bond character to the S-O bond, which will absorb at a shorter wave-length region.

Substituents other than those just discussed all have effect on the SO₂ group, but they cannot be discussed in detail since the spectra were measured in Nujol mull and the estimation of electronic shifts is rather complex. However, as the first approximation, a mean frequency $(\nu_{as} + \nu_s)/2$ which was proposed by Barnard³⁾ in the calculation of force constants may be used to compare with each other. This is also shown in Tables I and II, and it will be clear that the compounds which have similar substituents will have similar frequencies.

TABLE II. Infrared Absorption Bands of SO₂ Group in Phenylsulfonyl Derivatives

R ₃ - -SO ₂ -R ₁								
Compd. No.	R ₃	R ₁	State	$\nu_{as}^{a)}$			$\nu_s^{a)}$	Mean freq.
(XX)	HCl·H ₂ NCH ₂ ¹¹⁾	C ₂ H ₅	N	1316	1294	1279	1148	1232
(XXI)	HCl·H ₂ NCH ₂ CH ₂	C ₂ H ₅	N	1307	1279	1258	1136	1222
(XXII)	HCl·H ₂ N(CH ₃)CH	C ₂ H ₅	N	1314	1294	1274	1147	1231
(XXIII)	(CH ₃ CO ₂) ₂ CH ¹¹⁾	C ₂ H ₅	N	1319	1292		1151	1235
(XXIII)	(CH ₃ CO ₂) ₂ CH ¹¹⁾	C ₂ H ₅	C	1323			1148	1236
(XXIV)	CH ₃	C ₆ H ₅	N	1323	1311	1294	1157	1234
(XXV)	HCl·H ₂ NCH ₂	C ₆ H ₅	N	1314 ^{b)}	1305	1285	1156	1231
(XXVI)	P	C ₆ H ₅	N	1318	1309		1159	1238
(XXVII)	(CH ₃ CO ₂) ₂ CH ¹³⁾	C ₆ H ₅	N	1333	1318	1300	1166	1250
(XXVII)	(CH ₃ CO ₂) ₂ CH ¹³⁾	C ₆ H ₅	C	1325			1157	1241
(XXVIII)	HON=CH	C ₆ H ₅	N	1304	1287		1149	1218
(XXIX)	NH ₂	C ₆ H ₄ NH ₂ (<i>p</i>)	N	1295	1282		1143	1213
(XXX)	CH ₃	CH ₂ COOH	N	1326			1163	1245
(XXXI)	CN	CH ₂ COOH	N	1316 ^{b)}	1295		1156	1226
(XXXII)	H ₂ NCH ₂ ¹⁴⁾	CH ₂ COOH	N	1309	1299		1168	1239
(XXXIII)	P ¹⁴⁾	CH ₂ COOH	N	1321	1312 ^{b)}		1148 ^{b)} 1138	1230
(XXXIV)	CHO	CH ₂ COOH	N	1307	1300 ^{b)}	1276	1166	1237
(XXXV)	HON=CH	CH ₂ COOH	N	1316	1284		1149	1233
(XXXVI)	CN	CH ₂ COOC ₂ H ₅	N	1339			1156	1248
(XXXVII)	HCONHCH ₂ ¹⁴⁾	CH ₂ COOC ₂ H ₅	N	1328			1167	1248
(XXXVIII)	P ¹⁴⁾	CH ₂ COOC ₂ H ₅	N	1332			1147	1240
(XXXIX)	CN	CH ₂ COCH ₃	N	1332			1159 1148	1240
(XL)	H ₂ NCH ₂ ¹⁴⁾	CH ₂ COCH ₃	N	1326	1314 ^{b)}	1294	1155	1241
(XLI)	HCONHCH ₂ ¹⁴⁾	CH ₂ COCH ₃	N	1319	1300		1168 1149	1234
(XLII)	P ¹⁴⁾	CH ₂ COCH ₃	N	1330	1316 ^{b)}		1164	1247
(XLIII)	HCl·H ₂ NCH ₂ ¹⁴⁾	CH ₂ COC ₆ H ₅	N	1335 ^{b)}	1321	1304	1172	1247
(XLIV)	HCONHCH ₂ ¹⁴⁾	CH ₂ COC ₆ H ₅	N	1330 ^{b)}	1312	1290 ^{b)}	1161 1145	1229
(XLV)	HCl·H ₂ NCH ₂ ¹⁴⁾	C ₂ H ₄ OH	N	1311 ^{b)}	1295	1274 ^{b)}	1152 1142	1219

13) H. Burton, P. F. Hu: J. Chem. Soc., 1948, 601.

14) T. Momose, T. Shōji: Yakugaku Zasshi, 71, 681(1951).

(XLVI)	P ¹⁴⁾	C ₂ H ₄ OH	N	1295	1277	1138	1217
(XLVII)	H ₂ NCH ₂ ¹⁴⁾	CH ₂ J	N	1314	1297 ^{b)}	1152	1233
(XLVIII)	HCONHCH ₂ ¹⁴⁾	CH ₂ J	N	1318	1292 ^{b)}	1170	1148 1233
(XLIX)	P ¹⁴⁾	CH ₂ J	N	1325	1312	1302	1160 1143 1236
(L)	H	C ₆ H ₅	N	1324	1316	1300	1156 1236

a) Maximum absorption in bold-face type.

b) Shoulder.

N : Nujol.

C : CHCl₃ solution.

P : Phthaliminomethyl.

TABLE III. Shift of Mean Wave-number by the Substituent (R₁)

R ₃ - -SO ₂ -R ₁				
R ₁	R ₃	Mean wave number	Mean wave number of R ₁ =CH ₃	Shift
C ₂ H ₅	HCl·H ₂ NCH ₂	1232	1235	- 3
	HCl·H ₂ N(CH ₃)CH	1231	1230	+ 1
	(CH ₃ CO ₂) ₂ CH	1235	1235	0
	(CH ₃ CO ₂) ₂ CH	1236	1238	- 2 ^{a)}
C ₆ H ₅	CH ₃	1234	1227	+ 7
	HCl·H ₂ NCH ₂	1231	1235	- 4
	P	1238	1225	+13
	(CH ₃ CO ₂) ₂ CH	1250	1235	+15
	(CH ₃ CO ₂) ₂ CH	1241	1238	+ 3 ^{a)}
	HON=CH	1218	1230	-12
	H	1236	1214	+22
CH ₂ CO ₂ H	CH ₃	1245	1227	+18
	P	1230	1225	+ 5
	HON=CH	1233	1230	+ 3
CH ₂ CO ₂ C ₂ H ₅	CN	1248	1238	+10
	HCONHCH ₂	1248	1225	+23
	P	1240	1225	+15
CH ₂ COCH ₃	CN	1240	1238	+ 2
	HCl·H ₂ NCH ₂	1241	1235	+ 6
	HCONHCH ₂	1234	1225	+ 9
	P	1247	1225	+22
CH ₂ COC ₆ H ₅	HCl·H ₂ NCH ₂	1247	1235	+12
	HCONHCH ₂	1229	1225	+ 4
C ₂ H ₄ OH	HCl·H ₂ NCH ₂	1219	1235	-16
	P	1217	1225	- 8
CH ₂ I	HCONHCH ₂	1233	1225	+ 8
	P	1236	1225	+11

a) In CHCl₃ solution; others in Nujol.

P : Phthaliminomethyl.

Using this mean frequency the substitution effect of some substituents attached directly to the sulfonyl group was examined. This is shown in Table III. It is clear from the table that electron-accepting groups like C₆H₅, CH₂COOH, CH₂COOC₂H₅, CH₂COCH₃, CH₂COC₆H₅, and CH₂I give a stronger double-bond character to the S-O bond than CH₃ group, forcing it to absorb in a rather shorter wave-length region. Inversely electron-donating groups such as C₂H₅ and C₂H₄OH give a stronger single-bond character to the S-O bond which absorbs at a longer wave-length region. These results again confirm the fact that the inductive effect can affect the character of S-O bond and its absorption frequency, and therefore, the substituents attached to the phenyl ring or directly to the sulfonyl group take an important part in the S-O stretching vibration frequency.

Lastly, the apparent molecular extinction coefficients of four typical phenylsulfonyl-methane derivatives were measured in CHCl₃ solution. Though only the integrated intensities have theoretical significance, these apparent coefficients will be useful in

15) R.N. Jones, C. Sandorfy : "Chemical Applications of Spectroscopy," Technique of Organic Chemistry, Interscience Publ. Inc., U.S.A., IX, 271, 476(1956).

distinguishing some of the groups. Results show that the values are in a range of 481~774 (ϵ) for ν_{as} and of 932~1319 (ϵ) for ν_s . Barnard also reported that $\epsilon_{\text{max}}^{\text{CCl}_4}$ of ν_{as} and ν_s of sulfonyl group were in a range of 250~600 (ϵ) and of 500~900 (ϵ), respectively. Therefore, the maximum absorbancy of ν_s is roughly twice as strong as that of ν_{as} . Jones¹⁵ stated that the maximum absorbancy of organic compounds were between 1 and 1500 (ϵ), and the maximum molecular extinction coefficients of carbonyl bands lay in a range of 290~1335 (ϵ). The absorption band of sulfonyl group has strength comparable to that of carbonyl group, and the ν_s is more valuable for the identification of sulfonyl group, since the ν_{as} may have a larger chance of overlapping other frequencies and a smaller extinction coefficient.

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Experimental

Infrared Spectra—Measured with a Kōken Model DS-201 recording infrared spectrophotometer, using NaCl prism.

4-Phthalimidomethylphenylsulfonylbenzene (XXVI)—To a solution of 5 g. of 4-phthalimidomethylphenylsulfonyl chloride¹⁶ in 15 cc. of dry benzene, 5 g. of anhyd. AlCl_3 was slowly added under cooling. After the reaction ceased the solution was poured into ice water and precipitated crystals were recrystallized from AcOH to colorless prisms, m.p. 211~213°. *Anal.* Calcd. for $\text{C}_{21}\text{H}_{15}\text{O}_4\text{NS}$: N, 3.71. Found: N, 3.70.

4-Aminomethylphenylsulfonylbenzene Hydrochloride (XXV)—(XXVI) was heated for 15 hrs. in dehyd. EtOH with $\text{NH}_2\text{NH}_2 \cdot \text{H}_2\text{O}$. Separated phthalohydrazide was removed, EtOH was distilled off, and the residual solution was acidified with HCl. After removing insoluble substance while hot, crystals that appeared on cooling were recrystallized from EtOH to colorless plates, m.p. 250~252°. *Anal.* Calcd. for $\text{C}_{13}\text{H}_{14}\text{O}_2\text{NCIS}$: N, 4.93. Found: N, 5.04.

4-Hydroxyiminomethylphenylsulfonylbenzene (XXVIII)—Prepared from 4-formylphenylsulfonylbenzene,¹³ $\text{NH}_2\text{OH} \cdot \text{HCl}$, and AcONa. Recrystallization from EtOH yielded colorless prisms, m.p. 148~150°. *Anal.* Calcd. for $\text{C}_{13}\text{H}_{11}\text{O}_3\text{NS}$: N, 5.36. Found: N, 5.52.

The solution of (XXVIII) in 30% AcOH was reduced with Zn powder and treated as usual. Its hydrochloride formed colorless plates of m.p. 250~252° after recrystallization from EtOH, which showed no depression of mixed m.p. with (XXV).

3-Chloro-4-methylphenylsulfonylmethane—4-Methylphenylsulfonylmethane and calculated weight of Cl_2 gas gave colorless plates which crystallized from EtOH to crystals of m.p. 92°. *Anal.* Calcd. for $\text{C}_8\text{H}_9\text{O}_2\text{ClS}$: C, 46.93; H, 4.43. Found: C, 46.92; H, 4.45.

3-Chloro-4-diacetoxymethylphenylsulfonylmethane (XVII)—A solution of CrO_3 in 5 cc. of Ac_2O was added slowly under cooling to a solution of 5 g. of 3-chloro-4-methylphenylsulfonylmethane in 20 cc. of Ac_2O and maintained at 15~20°. After the reaction ceased it was poured into ice water and the separated oily substance was extracted with ether. The ether was evaporated and the residue was recrystallized from EtOH to colorless plates, m.p. 93~95°. *Anal.* Calcd. for $\text{C}_{12}\text{H}_{13}\text{O}_6\text{ClS}$: C, 44.93; H, 4.08. Found: C, 44.82; H, 3.83.

3-Chloro-4-formylphenylsulfonylmethane (XV)—(XVII) was saponified with ethanolic HCl. Recrystallization of its product from AcOEt yielded colorless needles, m.p. 137~138°. *Anal.* Calcd. for $\text{C}_8\text{H}_7\text{O}_3\text{ClS}$: C, 43.94; H, 3.22. Found: C, 44.02; H, 3.10.

3-Chloro-4-hydroxyiminomethylphenylsulfonylmethane (XIX)—Prepared from (XV), $\text{NH}_2\text{OH} \cdot \text{HCl}$, and Na_2CO_3 . Recrystallization from EtOH yielded colorless needles, m.p. 155~156°. *Anal.* Calcd. for $\text{C}_8\text{H}_8\text{O}_3\text{NCIS}$: N, 5.74. Found: N, 5.98.

3-Chloro-4-aminomethylphenylsulfonylmethane Hydrochloride (IX)—(XIX) was reduced with AcOH and Zn powder, and its hydrochloride was recrystallized from EtOH to colorless plates, m.p. 265°. *Anal.* Calcd. for $\text{C}_8\text{H}_{11}\text{O}_2\text{NCl}_2\text{S}$: N, 5.46. Found: N, 5.68.

4-Cyanophenylsulfonylacetone (XXXIX)—Two g. of chloroacetone was added to a solution of 4 g. of sodium 4-cyanophenylsulfinate¹⁷ in 20 cc. of water, and the mixture was refluxed for 2 hrs. On cooling crystals separated which were recrystallized from EtOH to colorless needles of m.p. 112~113°. Yield, 4 g. *Anal.* Calcd. for $\text{C}_{10}\text{H}_9\text{O}_3\text{NS}$: N, 6.28. Found: N, 6.22.

16) M. Kusami, K. Yamaguchi, S. Yamaguchi: *Yakugaku Zasshi*, **64**, 240(1944).

17) A. T. Fuller, I. M. Tonkin, J. Walker: *J. Chem. Soc.*, **1945**, 633.

Ethyl 4-Cyanophenylsulfonylacetate (XXXVI)—Two g. of ethyl chloroacetate was added to a solution of 4 g. of sodium 4-cyanophenylsulfinate in 20 cc. of water and the mixture was refluxed for 3 hrs. Recrystallization of the separated crystals from EtOH yielded colorless needles of m.p. 70°. Yield, 4 g. *Anal.* Calcd. for $C_{11}H_{11}O_4NS$: N, 5.53. Found: N, 5.39.

4-Formylphenylsulfonylacetate (XXXIV)—To a solution of 5 g. of 4-methylphenylsulfonylacetate in a mixture of 20 cc. of Ac_2O and 5 cc. of conc. H_2SO_4 , 4 g. of CrO_3 dissolved in 8 cc. of Ac_2O was dropped in under stirring at 10–15°. After the reaction ceased the mixture was poured into ice water, the separated oily substance was heated with 20 cc. of 10% HCl for a while, and crystals that separated after cooling were recrystallized from EtOH to colorless plates, m.p. 150–152°. Yield, 3.5 g. *Anal.* Calcd. for $C_9H_8O_5S$: C, 47.38; H, 3.53. Found: C, 47.24; H, 3.83.

4-Hydroxyiminomethylphenylsulfonylacetate (XXXV)—Prepared from (XXXIV), $NH_2OH \cdot HCl$, and NaOH. Recrystallization from water yielded colorless needles of m.p. 205°(decomp.). *Anal.* Calcd. for $C_9H_8O_5NS$: N, 5.76. Found: N, 5.85.

4-Diacetylaminophenylsulfonylmethane (VII)—4-Acetamidophenylsulfonylmethane (VI) of m.p. 190° was converted to diacetyl derivative by refluxing with Ac_2O for several hrs. After distillation of Ac_2O in vacuum, MeOH and water were added and separated crystals were recrystallized from dil. MeOH to colorless needles of m.p. 152–153°. *Anal.* Calcd. for $C_{11}H_{13}O_4NS$: C, 51.76; H, 5.13. Found: C, 51.87; H, 5.26.

When dil. NaOH was added to a solution of (VII) in EtOH and kept at room temperature, (VI) separated as crystals of m.p. 190°.

4-Diacetylaminomethylphenylsulfonylmethane (XIII)—Prepared from (XII) similarly as above. Recrystallization from dil. MeOH gave colorless needles of m.p. 140°. *Anal.* Calcd. for $C_{12}H_{15}O_4NS$: N, 5.49. Found: N, 5.00.

Summary

Infrared spectra of 50 phenylsulfonyl derivatives were measured and substituent effect on the sulfonyl group was discussed. Inductive and mesomeric effects of substituents attached to the phenyl ring or directly to the sulfonyl group somewhat affected the frequencies of asymmetric and symmetric stretching vibrations of SO_2 . The frequency shifts had some correlations with Hammett's σ -value of the chemical shifts of benzene derivatives. Synthesis of some phenylsulfonyl derivatives is also described.

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81. Masaharu Yamagishi and Isao Nakamura: Studies on Determination of Sapogenins in Plants belonging to *Dioscorea* growing in Japan. II.¹⁾ Determination of Diosgenin, Tokorogenin, and a New Genin contained in the Roots.

(Research Laboratories, Takeda Pharmaceutical Industries, Ltd.*)

In Part I of this series,¹⁾ the authors announced that a new color reaction of diosgenin and tokorogenin satisfies Beer's law and is available for colorimetric determination of these genins. In the present work a method for determining the sapogenins present in roots of *Dioscorea Tokoro* MAKINO and *D. nipponica* M. was established utilizing the above color reaction. As a new genin was found in the sapogenin extract of *D. Tokoro* M. (X-substance**), the present method was studied centering on the separatory determination of diosgenin, tokorogenin, and the X-substance. The main procedures of this method are as follows:

1) Part I: Yakugaku Zasshi, 78(1958) in press.

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** Morita in this Laboratories found that this substance is identical with yonogenin, m.p. 238–240°, $\alpha_D -63^\circ$ (cf. K. Takeda, *et al.*: Yakugaku Zasshi, 77, 822(1957)).