dration or mercaptan or sulfide formation. Unfortunately, the carbon-sulfur vibrations are relatively weak and occur at 600–700 cm.$^{-1}$ region, which was not readily accessible with the equipment available in this laboratory.

Lignosulfonates. The spectral shift observed upon conversion of sodium and calcium lignosulfonates to free lignosulfonic acids by ion exchange indicated the presence of carboxyl groups in lignosulfonates, although the amount appears to be less than that present in kraft lignins. Unconjugated carbonyl groups are absent and conjugated carbonyl groups are present in relatively small amount, except in lignosulfonates which have been treated with alkali. In the latter case, an appreciable content of ketone carbonyl groups conjugated with a free *para*-hydroxyl group is indicated.

The absorption bands in the lignosulfonic acid spectrum, as compared to dioxane–hydrochloric acid lignin, are rounded or less well defined. The 815 and 860 cm.$^{-1}$ bands are very weak. This strongly suggests higher molecular weights (increases in molecular weight usually produce a more diffuse spectrum), structural rearrangement and/or condensation. Colthup[31] suggests the following series of absorption bands for sulfonic acids and salts: 1260–1150 cm.$^{-1}$ (strong), 1080–1010 cm.$^{-1}$ (medium) and 600–700 cm.$^{-1}$ (medium). A strong but broad band at 1200–1210 cm.$^{-1}$, a band at 1040 cm.$^{-1}$ (evidenced by markedly increased absorption at this wave length as compared with dioxane–hydrochloric acid lignin), and a medium intensity band at 650 cm.$^{-1}$ were observed in the lignosulfonic acid. The band at 1200–1210 cm.$^{-1}$ is somewhat more pronounced in the lignosulfonate salt. Both the 1210 and 1040 cm.$^{-1}$ bands occur at the same frequency as absorption bands already present in the unsulfonated lignin molecule, so they are not particularly valuable for diagnostic studies. The 650 cm.$^{-1}$ band does not occur in unsulfonated lignin. Desulfonation of a sodium lignosulfonate by treatment with sodium hydroxide at elevated temperatures results in a loss of the 650 cm.$^{-1}$ band and a marked decrease in the 1040 and 1210 cm.$^{-1}$ absorptions. The spectrum of the desulfonated lignosulfonate, though containing bands of approximately the same wave lengths, is readily distinguishable from the dioxane lignin spectrum. Considerable structural alteration has apparently occurred in the desulfonation process, including increase in phenolic hydroxyl content and loss of methoxyl groups.

Although considerable information about the structure of conifer lignin has been gained by a study of their infrared spectra, the work reported here also indicates that elucidation of lignin structure may be even more difficult than hitherto suspected. Thus, not only are native lignins not identical with whole wood lignin, but lignin structure appears to vary with genera. Further difficulties are involved in the fact that many previous investigators have attempted to apply their results on lignins isolated by processes such as alcoholysis, sulfonation, etc., to lignin as it exists in wood. Infrared spectra show, however, that many of these lignins are rearranged during isolation; consequently structural studies based on them are of limited value for this purpose. Since generic differences in lignins are apparent from the spectra, it is proposed that future work should be devoted to functional group analyses of lignins isolated by the same process from various genera, and that the enzyme systems and cambial constituents (lignin intermediates) of various genera and species be compared. In this way many past discrepancies in the lignin literature are likely to be clarified.

(31) N. Colthup, *J. Opt. Soc. America*, **40**, 397 (1950).

SHELTON, WASHINGTON

[CONTRIBUTION FROM THE LILLY RESEARCH LABORATORIES]

The Reaction of Saccharin with Amines. *N*-Substituted-3-Amino-1,2-benzisothiazole-1,1-dioxides

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Saccharin reacts with excess amines to produce *N*-substituted 3-amino-1,2-benzisothiazole-1,1-dioxides. Under the same conditions *N*-methylsaccharin produces *N*-substituted *o*-methylsulfamylbenzamides. Saccharin with one equivalent of amine produces *N*-substituted *o*-sulfamylbenzamides. The reaction products of hydrazine hydrate with saccharin and *N*-methylsaccharin have been assigned structures based on the similarity of their infrared spectra to that of benzoic acid hydrazide.

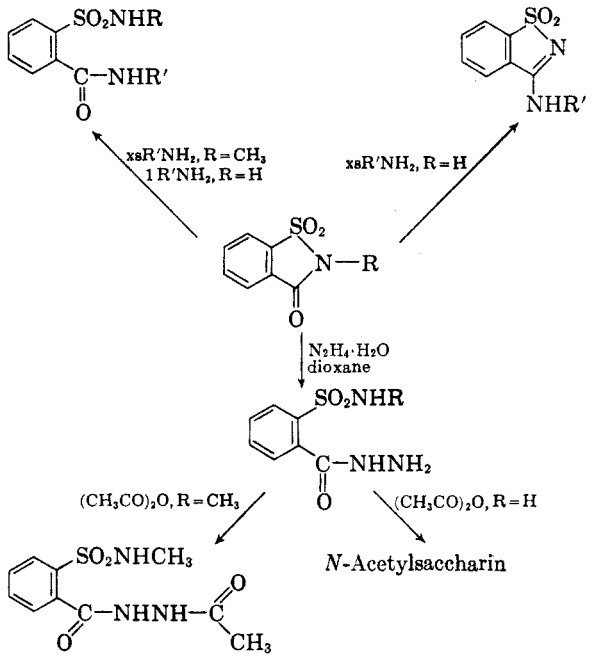
A number of 3-amino-1,2-benzisothiazole-1,1-dioxides were prepared for pharmacological evaluation as diuretic or hypoglycemic agents. As in the case of arylamines,[1] refluxing saccharin with alkyl- and aralkylamines boiling at least at 130° for eight hours gave crystalline 3-amino-1,2-benzisothiazole-1,1-dioxides. Derivatives of lower boiling amines

(1) A. Mannessier-Mameli, *Gazz. chim. ital.*, **65**, 51 (1935); *Chem. Abstr.*, **29**, 3996 (1935).

were made by the amination of pseudosaccharin chloride. These compounds are all weak acids with pK'_a values of about 12.5 in 66% dimethylformamide. All the 3-amino-1,2-benzisothiazole-1,1-dioxides have a bitter taste.

Under the conditions which produced the 3-amino-1,2-benzisothiazole-1,1-dioxides, *N*-methylsaccharin yielded benzamide derivatives. *N*-substituted *o*-methylsulfamylbenzamides were obtained when *N*-methylsaccharin was refluxed with excess amines boiling at least at 130°. The *N*-substituted *o*-sulfamylbenzamides were prepared by refluxing saccharin with one equivalent of amine in chlorobenzene solvent. The *o*-sulfamylbenzamides are weakly acidic with pK'_a values of 12.4 while the *o*-methylsulfamylbenzamides have pK'_a values of 13.3 in 66% dimethylformamide.

A similar situation occurred when hydrazine hydrate was used as a reactant under milder conditions. In aqueous solution saccharin and hydrazine hydrate merely formed the salt. In dioxane, saccharin and hydrazine hydrate produced a compound with the empirical formula $C_7H_9N_3O_3S$ after initial salt formation. *N*-Methylsaccharin also reacted with hydrazine hydrate in dioxane to give a product of $C_8H_{11}N_3O_3S$.



The infrared spectra of the two compounds are very similar and suggest like structures. In acetonitrile solution $C_8H_{11}N_3O_3S$ shows amide carbonyl absorption (1658 cm.$^{-1}$), NH_2 deformation (*ca.* 1635 cm.$^{-1}$), amide II (1520 cm.$^{-1}$) and SO_2 stretching absorption (1337, 1175 cm.$^{-1}$). $C_7H_9N_3O_3S$ exhibits amide carbonyl absorption (1660 cm.$^{-1}$), NH_2 deformation (1637 cm.$^{-1}$), amide II (1527 cm.$^{-1}$) and SO_2 stretching absorption (1353, 1173 cm.$^{-1}$). The hydrazine hydrate reaction product of *N*-methylsaccharin ($C_8H_{11}N_3O_3S$) was assigned the structure *o*-methylsulfamylbenzoylhydrazine because of the similarity of the infrared spectrum to that of benzoic acid hydrazide. The solution spectrum (chloroform) of $C_8H_{11}N_3O_3S$ contains NH stretching absorption (3440, 3342, ca. 3285 cm.$^{-1}$), amide carbonyl (1667 cm.$^{-1}$), amide II (1467 cm.$^{-1}$), NH_2 deformation (1625 cm.$^{-1}$) and SO_2 absorption (1337 and 1170 cm.$^{-1}$). In chloroform solution benzoic acid hydrazide exhibits NH absorption (3460, 3340 cm.$^{-1}$), amide carbonyl (1670 cm.$^{-1}$), amide II (1478 cm.$^{-1}$) and NH_2 deformation absorption (1627 cm.$^{-1}$). The shapes and relative intensities of these bands are comparable. Removal of the amide NH and NH_2 deformation bands in the spectra of the deuterated compounds (prepared by exchange with deuterium oxide) establishes the correctness of these assignments. Thus the hydrazine hydrate reaction product of saccharin ($C_7H_9N_3O_3S$) is *o*-sulfamylbenzoylhydrazine.

o-Sulfamylbenzoylhydrazine has an acidic pK'_a 12.0 in 66% dimethyl formamide whereas *o*-methylsulfamylbenzoyl-hydrazine has pK'_a 12.7. Alkyl substitution on the sulfamyl group decreases the acid strength as exemplified by *N*-cyclohexyl-*o*-sulfamylbenzamide (pK'_a 66% dimethylformamide 12.4) and *N*-cyclohexyl-*o*-methylsulfamylbenzamide (pK'_a 66% dimethylformamide 13.3). Although both benzoic acid hydrazide and benzenesulfonamide are weakly acidic (pK'_a 66% dimethylformamide *ca.* 14.0, 13.1), the group titrated in the *o*-sulfamylbenzoyl hydrazines must represent the acidic dissociation of the sulfamyl group. Alkyl substitution on the sulfamyl group would not be expected to lower the acidity of the acid hydrazide.

Both *o*-sulfamylbenzoylhydrazines were treated with acetic anhydride under mild conditions. *o*-Methylsulfamylbenzoylhydrazine produced a normal derivative, 1-acetyl-2-(*o*-methylsulfamylbenzoyl) hydrazine (pK'_a 66% dimethylformamide 10.0). Acetylation of benzoic acid hydrazide greatly increases the acidity (1-acetyl-2-benzoylhydrazine, pK'_a 66% dimethylformamide 11.3). *o*-Sulfamylbenzoylhydrazine, however, produced a cleavage product identified as *N*-acetylsaccharin.

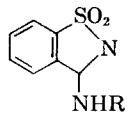
EXPERIMENTAL

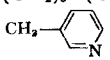
N-Substituted-3-amino-1,2-benzisothiazole-1,1-dioxides (Table I). *Method A.* One-tenth mole of saccharin was added to excess alkyl- or aralkylamine boiling at least at 130°. After initial salt formation the saccharin went into solution and refluxing was continued for 8 hr. The excess amine was then removed under reduced pressure and ether was added to the residue. The crystalline product was collected and again washed with ether. When it was difficult to remove high boiling amines, ether was added directly to the cooled reaction mixture and the crystalline product was filtered off. The 3-amino-1,2-benzisothiazole-1,1-dioxides were purified by crystallization from ethanol or aqueous ethanol.

Method B. Pseudosaccharin chloride[2] (0.05–0.10 mole)

(2) J. R. Meadow and E. E. Reid, *J. Am. Chem. Soc.*, **65**, 457 (1943).

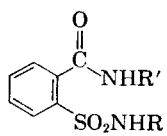
TABLE I. *N*-SUBSTITUTED 3-AMINO-1,2-BENZISOTHIAZOLE-1,1-DIOXIDES

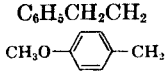
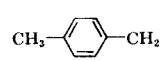


R	Formula	M.P.	Yield, %[a]	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
CH_3	$C_8H_8N_2O_2S$	292 dec.	25 B	48.96	49.09	4.11	4.29	14.28	14.33
CH_2CH_2OH	$C_9H_{10}N_2O_3S$	238	31 A	47.77	47.55	4.45	4.42	12.38	12.58
n-C_3H_7	$C_{10}H_{12}N_2O_2S$	215	61 B	53.55	53.32	5.39	5.36	12.49	12.49
iso-C_5H_{11}	$C_{12}H_{16}N_2O_2S$	166	20 B	57.11	57.31	6.39	6.35	11.10	11.24
$(CH_2)_3N(CH_3)_2$	$C_{12}H_{17}N_3O_2S$	150[b]	41 A	53.91	53.90	6.41	6.54	15.72	15.57
	$C_{13}H_{11}N_3O_2S$	224	55 A	57.13	57.10	4.06	3.97	15.38	15.09
cyclohexyl	$C_{13}H_{16}N_2O_2S$	248	40 A	59.06	59.08	6.10	6.09	10.60	10.68
$CH_2C_6H_5$	$C_{14}H_{12}N_2O_2S$	209	55 A	61.74	62.31	4.44	4.46	10.29	10.30
$CH_2CH_2C_6H_5$	$C_{15}H_{14}N_2O_2S$	244	52 A	62.91	62.92	4.93	4.94	9.78	10.04
p-$CH_3C_6H_4CH_2$	$C_{15}H_{14}N_2O_2S$	222	56 A	62.91	62.44	4.93	5.30	9.78	9.79
m-$CH_3C_6H_4CH_2$	$C_{15}H_{14}N_2O_2S$	214	55 A	62.91	62.87	4.93	4.98	9.78	9.81
p-$CH_3OC_6H_4CH_2$	$C_{15}H_{14}N_2O_3S$	209	46 A	59.58	59.40	4.66	4.48	9.27	9.10

[a] A, Prepared by Method A; B, prepared by Method B. [b] Crystallized from benzene.

TABLE II. *N*-SUBSTITUTED-*o*-SULFAMYLBENZAMIDES



R	R′	Formula	M.P.	Yield, %	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found	Nitrogen Calcd.	Nitrogen Found
H	cyclohexyl	$C_{13}H_{18}N_2O_3S$	196	21	55.29	55.52	6.42	6.62	9.92	9.63
H	$C_6H_5CH_2$	$C_{14}H_{14}N_2O_3S$	103	31	57.93	57.74	4.86	4.63	9.65	9.67
CH_3	cyclohexyl	$C_{14}H_{20}N_2O_3S$	130	53	56.73	56.97	6.80	6.71	9.45	9.18
CH_3	$C_6H_5CH_2$	$C_{15}H_{16}N_2O_3S$	105	33	59.19	59.39	5.30	5.63	9.20	9.14
H	$C_6H_5CH_2CH_2$	$C_{15}H_{16}N_2O_3S$	108	20	59.19	59.41	5.30	5.06	9.20	8.82
H		$C_{15}H_{16}N_2O_4S$	115	15	56.23	56.44	5.03	5.14	8.74	8.75
CH_3		$C_{16}H_{18}N_2O_3S$	104	49	60.35	60.39	5.70	6.02	8.80	8.53

was added portionwise to two equivalents of the appropriate amine in dioxane. The mixture was then heated on the steam bath for 1 hr. The dioxane was removed under reduced pressure and dilute ethanol was added to the residue. The solution was treated with carbon if necessary and then filtered. The products were crystallized by concentrating the solution and cooling. The 3-amino-1,2-benzisothiazole-1,1-dioxides were purified by crystallization from ethanol or aqueous ethanol.

N-Substituted-o-sulfamylbenzamides (Table II). Saccharin (0.10–0.20 mole) was added to chlorobenzene to which one equivalent of the appropriate amine had been added. The mixture was refluxed for 8 hr. and then the solvent was removed under reduced pressure. The residue was acidified by the addition of dilute hydrochloric acid and cooled. The material which crystallized was collected and recrystallized from dilute ethanol. The *o*-sulfamylbenzamides were purified by crystallization from aqueous ethanol.

N-Substituted-o-methylsulfamylbenzamides (Table II). *N*-Methylsaccharin[3] (0.05–0.10 mole) was added to excess alkyl- or aralkylamine boiling at least at 130°. The mixture was refluxed for 8 hr. and then as much of the excess amine as possible was removed under reduced pressure. Dilute hydrochloric acid was added to the residue and the acidic solution was cooled to induce crystallization. The material which crystallized was collected and recrystallized from dilute ethanol. The *o*-methylsulfamylbenzamides were purified by crystallization from aqueous ethanol.

o-Sulfamylbenzoylhydrazine. Eighteen grams (0.10 mole) of saccharin was heated on the steam bath for 5 hr. with 5 g. (0.10 mole) of 100% hydrazine hydrate in 250 ml. of dioxane. After the mixture had become homogeneous most of the dioxane was removed under reduced pressure and the crystalline residue was collected. The product was crystallized from ethanol to yield 16.5 g. (77%) of material. The *o*-sulfamylbenzoylhydrazine was purified by crystallization from ethanol, m.p. 180° dec.

Anal. Calcd. for $C_7H_9N_3O_3S$: C, 39.06; H, 4.21; N, 19.53. Found: C, 39.06; H, 4.10; N, 19.81.

o-Methylsulfamylbenzoylhydrazine. Twenty grams (0.10 mole) of *N*-methylsaccharin was added to 150 ml. dioxane. Five grams (0.10 mole) of 100% hydrazine hydrate was added to the solution and the mixture was heated on the steam bath for 4 hr. The dioxane was removed under reduced pressure and the residue was dissolved in ethanol and filtered. The product was crystallized by concentrating the ethanol solution and cooling. The *o*-methylsulfamylbenzoylhydrazine was purified by crystallization from ethanol to yield 17 g. (74%) of material, m.p. 140°.

Anal. Calcd. for $C_8H_{11}N_3O_3S$: C, 41.91; H, 4.84; N, 18.33. Found: C, 42.04; H, 4.92; N, 18.18.

N-Acetylsaccharin. Five grams of *o*-sulfamylbenzoylhydrazine was warmed on the steam bath with 40 ml. acetic anhydride to dissolve the solid. The mixture was allowed to stand overnight at room temperature. The excess acetic anhydride was removed under reduced pressure and the residue was dissolved in ethanol. The ethanol solution was concentrated and cooled to yield 3 g. of material with m.p. 191° (lit.[4] m.p. 193°) after recrystallization from ethanol. The infrared spectrum of this material was identical with that of an authentic sample of *N*-acetylsaccharin.

Anal. Calcd. for $C_9H_7NO_4S$: C, 48.00; H, 3.12; N, 6.23. Found: C, 47.84; H, 2.82; N, 6.07.

1-Acetyl-2-(o-sulfamylbenzoyl)hydrazine. Five grams of *o*-methylsulfamylbenzoylhydrazine was warmed on the steam bath with 35 ml. acetic anhydride and then allowed to stand overnight at room temperature. The excess acetic anhydride was removed under reduced pressure and the residue was dissolved in ethanol. Concentration of the solution and cooling yielded 3.5 g. of material. The 1-acetyl-2-(*o*-sulfamylbenzoyl)hydrazine was recrystallized from ethanol m.p. 164°.

Anal. Calcd. for $C_{10}H_{13}N_3O_4S$: C, 44.27; H, 4.83; N, 15.49. Found: C, 44.17; H, 4.97; N, 15.78.

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INDIANAPOLIS, IND.

(3) H. L. Rice and G. R. Pettit, *J. Am. Chem. Soc.*, **76**, 302 (1954).

(4) H. Eckenroth, *Chem. Zentr.*, I, 235 (1897).

[CONTRIBUTION NO. 1587 FROM THE DEPARTMENT OF CHEMISTRY, YALE UNIVERSITY]

Electron Exchange Polymers. XIII. The Preparation of β-Vinylanthraquinone[1]

MIGUEL FERNANDEZ-REFOJO, YUE-LIANG PAN, KENNETH A. KUN, AND HAROLD G. CASSIDY

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The synthesis of β-vinylanthraquinone (2-ethenylanthraquinone) from 2-methylanthraquinone is described. 2-Methylanthraquinone is oxidized to the 2-aldehyde which is converted to anthraquinone-2-acrylic acid. This yields β-vinylanthraquinone upon decarboxylation. The vinyl compound is characterized by physical and chemical methods. It appears possible to polymerize the vinyl compound and to prepare copolymers with styrene, with α-methylstyrene, and with maleic anhydride using free-radical initiators. The yields are low, and the products have not been characterized.

Anthraquinone has been shown not to interrupt the polymerization of styrene, as the presence of anthraquinone during polymerization has no effect on the molecular weight of the polystyrene produced.[2] Anthraquinone is also reported not to react with free radicals from azodiisobutyronitrile.[3] Moreover, three vinylanthracenes have been pre-

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(2) B. A. Dolgoplosk and S. Sh. Korotkina, *Zhur. Obshcheĭ Khim.*, **27**, 2546 (1957). (Through *Chem. Abstr.*, **52**, 7218[i].)

(3) F. J. L. Aparicio and W. A. Waters, *J. Chem. Soc.*, **1952**, 4666.