ture was evaporated, the residue was chilled, and acidified with conc. HCl. The yellow precipitate was collected and recrystallized twice from EtOH; m.p. 223°. *Anal.* Calcd. for $C_{11}H_{11}O_2N_4ClS$: C, 44.52; H, 3.71. Found: C, 44.23; H, 3.98.

3-Sulfanylamido-5-methyl-6-methoxypridazine (III) and 3-Sulfanylamido-5-methyl-6-hydroxypridazine (II)—To a MeOH solution of MeONa (0.12 g. of Na dissolved in 15 cc. of MeOH), 0.6 g. of (I) was added and the mixture was heated in a sealed tube at 130~140° for 8 hrs. After cool, the reaction mixture was filtered, acidified with 10% AcOH under ice-cooling, and evaporated to dryness. The residue was dissolved in 5% NaOH, chilled, and acidified with 10% AcOH. The crude product was collected and recrystallized from MeOH to give 3-sulfanylamido-5-methyl-6-methoxypridazine, m.p. 182°.

In the above-mentioned reaction, 3-sulfanylamido-5-methyl-6-hydroxypridazine was obtained as colorless leaflets, m.p. 242°, when the temperature was at 40~60° during acidification.

3-Sulfanylamido-5-methyl-6-alkoxypyridazines (IV~X)—To an alcoholic solution of sodium alkoxides (0.01 mole of Na dissolved in 10~15 cc. of the alcohol) 1.16 g. of (I) was added and the reaction mixture was heated in a sealed tube at 130~150° for 8~13 hrs. After cool, the mixture was filtered, acidified with 10% AcOH, and evaporated to dryness. The residue was dissolved in 5% NaOH, chilled, and acidified with 10% AcOH. The crude product was collected and, recrystallized from EtOH or water-EtOH (see Table I).

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Noboru Takahayashi and Rikuko Honda: Synthesis of Pyridazine Derivatives. IX.[1] On the Oxidation Products of Sulfur-containing Compounds of Pyridazine. (3).[2]

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In one of the previous papers[2] of this series, one of the present authors (N.T.) reported the oxidation of 3-chloro-6-alkylthiopyridazine (I). It was at first assumed that the oxidation product obtained from (I) with peracetic acid might be its N-oxide.

A more extensive studies, especially on the oxidation products of 3-chloro-6-methylthio-, -6-ethylthio-, and -6-isopropylthio-pyridazines revealed that they are 6-alkylsulfonyl-3-pyridazinols (II) and it was further clarified that 3-methoxy-6-alkylthio- and 3-phenoxy-6-alkylthio-pyridazines also produced corresponding (II) with peracetic acid.

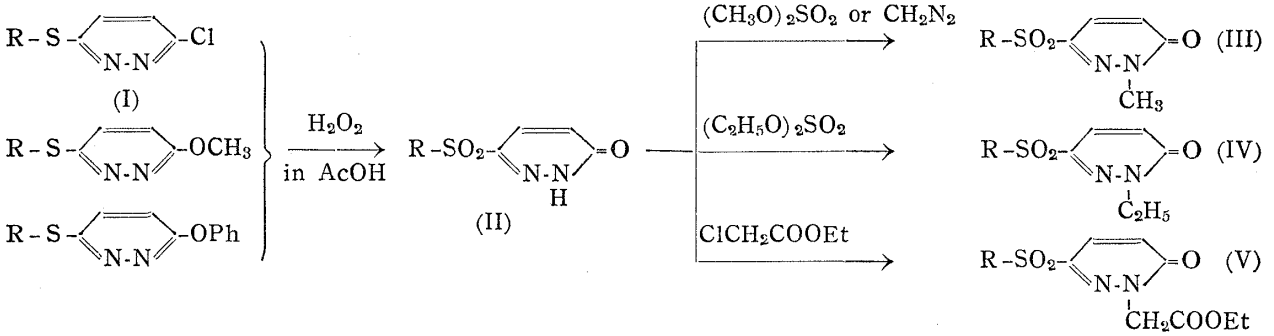

Chart 1. R=(a) CH_3, (b) C_2H_5, (c) *iso*-C_3H_7

Infrared absorption spectra of (IIa) and (IIb) support the formula (II), namely, as listed in Table I, they exhibit absorptions of C=O, N-H, and S-O.

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1) Part VIII: This Bulletin, **5**, 229 (1957).

2) Part IV: Yakugaku Zasshi, **75**, 1245 (1955); Part VI: *Ibid.*, **76**, 1293 (1956).

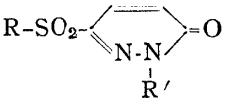
TABLE I. Infrared Absorption Spectra of (II) (μ in Nujol)

	$\nu_{C=O}$	ν_{N-H}	ν_{S-O}
(IIa)	6.13	3.50	8.83
(IIb)	6.12	3.50	8.85

Methylation or ethylation of (II) with dimethyl or diethyl sulfate yielded corresponding 1-methyl-6-alkylsulfonylpyridazinol (III) or 1-ethyl-6-alkylsulfonylpyridazinol (IV). Methylation with diazomethane also produced (III). On the other hand, an isomer of (IIIa), 3-methoxy-6-methylsulfonylpyridazine, was obtained by reaction of sodium methoxide with 3-chloro-6-methylsulfonylpyridazine.[3]

Moreover, ethyl 6-oxo-3-alkylsulfonyl-1,6-dihydro-1-pyridazine acetate (V) was prepared from (II) with ethyl chloroacetate in anticipation of sedative effect.

The maximum absorption wave-length in ultraviolet absorption spectra of these compounds are listed in Table II.

TABLE II. 2-Substituted 6-Alkylsulfonyl-3-pyridazinols $R\text{-}SO_2$- 

No.	R	R′	m.p. (°C)	Crystal form[a]	Analysis (%) Calcd. C	Calcd. H	Found C	Found H	UV-spectra (λ_{max} mμ) (in EtOH)
(IIa)	CH_3	H	202	leaflets	34.47	3.47	34.45	3.69	**237.5**, 295. (in 0.1*N* HCl; **208**, 237, 288: in 0.1*N* NaOH; 211, **236**, 288)
(IIb)	C_2H_5	〃	151	〃	38.29	4.29	38.45	4.51	**237.5**, 295. (in 0.1*N* HCl; **210**, 237, 288: in 0.1*N* NaOH; 211, **235**, 285)
(IIc)	*iso*-C_3H_7	〃	144	〃	41.57	4.98	41.16	4.86	**237.5**, 295.
(IIIa)	CH_3	CH_3	159.5	plates	38.29	4.29	38.31	4.39	**219**, 237, 300.[b]
(IIIb)	C_2H_5	〃	99.5	needles	41.57	4.98	41.39	5.10	**219**, 237, 260, 300.
(IIIc)	*iso*-C_3H_7	〃	131.5	leaflets	44.41	5.59	44.13	5.88	**219**, 237, 260, 300.
(IVa)	CH_3	C_2H_5	91.5～92.5	needles	41.57	4.98	41.47	5.07	**219**, 237, 260, 300.
(IVb)	C_2H_5	〃	55[c]	prisms	44.41	5.59	44.45	5.60	**219**, 237, 260, 300.
(IVc)	*iso*-C_3H_7	〃	97～98.5	plates	46.93	6.13	46.54	6.21	**219**, 237, 260, 300.
(Va)	CH_3	CH_2COOEt	96～96.5	needles	41.53	4.65	41.65	4.75	**219**, 255, 298.
(Vb)	C_2H_5	〃	51.5[d]	prisms	43.99	5.12	44.11	5.22	**219**, 255, 295.
(Vc)	*iso*-C_3H_7	〃	88～89.5	〃	45.82	5.59	45.80	5.64	**219**, 255, 298.

a) All compounds are colorless. b) The isomer of (IIIa), 3-methoxy-6-methylsulfonylpyridazine, possesses the absorption maxima at 227.5, **272.5**, and 321 mμ. c) b.$p_{0.0005}$ 120～125°. d) b.$p_{0.002}$ 118～123°.

The authors wish to express their appreciation to Professor D. Shiho for his kind advice and to Assist. Professor M. Yamaguchi, Medical College of Wakayama, for infrared measurements.

Experimental

The reactions described below are common to methyl-, ethyl-, and isopropyl-sulfonyl compounds.

Preparation of 6-Alkylsulfonyl-3-pyridazinol (II)—To a solution of 3-chloro-, 3-methoxy-, or 3-phenoxy-6-alkylthiopyridazine in glacial AcOH, 3～5 equivalents of H_2O_2 was added and the mixture was heated in a water bath at 70～80° for 3～6 hrs. The solution was concentrated to about one-half the original volume, diluted with water, and again concentrated in vacuum as much as possible. The residue was recrystallized several times from EtOH.

Reaction of (II) with Dimethyl or Diethyl Sulfate—To a suspension of (II) in water, containing a drop of phenolphthalein, a solution of 20% NaOH was added dropwise, with stirring, until the suspended material just dissolved and the solution became alkaline. Under stirring, Me_2SO_4 or Et_2SO_4 (1.1 equiv.) was introduced in small portions together with additional 20% NaOH to maintain the medium alkaline. The mixture was then warmed at 50～60° for 30 mins. The solid that deposited was collected and

3) Part VII: Yakugaku Zasshi, **76**, 1296 (1956).

recrystallized from EtOH. If a solid did not deposit, the reaction mixture was extracted with benzene and, after removal of benzene, the residue was recrystallized from EtOH to give 2-methyl-6-alkylsulfonyl-3-pyridazinol (III) or 2-ethyl-6-alkylsulfonyl-3-pyridazinol (IV).

Methylation of (II) with Diazomethane.—To an ethereal solution of CH_2N_2 powdered (II) was added and after evolution of nitrogen had subsided, the reaction mixture was placed in a refrigerator for 24 hrs. The solid that deposited was collected and recrystallized from EtOH to give corresponding 2-methyl-6-alkylsulfonyl-3-pyridazinol (III).

Reaction of (II) with Ethyl Chloroacetate—To a solution of (II) dissolved in 15 cc. of aq. solution of 1.1 equiv. K_2CO_3, ethyl chloroacetate (1.1 equiv.) was added dropwise with stirring. The mixture was warmed at 60～70° for 30 mins. and extracted with benzene. After removal of benzene, the residue was recrystallized from EtOH to give ethyl 6-oxo-3-alkylsulfonyl-1,6-dihydro-1-pyridazine acetate (V).

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Kyosuke Tsuda, Saburo Akagi, Yukichi Kishida, Ryoichi Hayatsu und Kiyoshi Sakai:

Untersuchungen über Steroide. IX. Die Sterine aus Meeres-algen.

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In den vorherigen Mitteilungen[1～4] dieser Reihe haben wir Isolierung, Charakterisierung und Strukturbeweis der Sterine aus Meeres-algen beschrieben. Diese Untersuchungen können im folgenden kurz zusammengefasst werden: (1) Aus verschiedenen Gattungen der Braunalgen wurde meistens nur das Fucosterin isoliert. Eine Algen-art in der *Sargassum*-Gattung aber, gab ein neues Sterin, das Sargasterin, dessen Struktur durch Abbaureaktionen[1] und synthetischen Versuche[2] eindeutig aufgeklärt und als das 20-Isofucosterin formuliert wurde. (2) Die geprüften Rotalgen, die auch zur verschiedenen Gattungen gehörten, gaben ausnahmslos das Cholesterin. Aus einigen Arten konnte neben Cholesterin das Chalinasterin isoliert werden.[3,4]

Es erscheint uns von Interesse, diese Untersuchungen weiter durchzuführen und so einerseits das allgemeine Vorkommen des Cholesterins in anderen Rotalgen nachzuweisen und andererseits das Sargasterin aus anderen Braunalgen zu gewinnen.

In der vorliegenden Arbeit berichten wir über Untersuchungen, die wir zu diesem Zweck durchzuführen. Zur Reinigung des rohen Sterins verwendeten wir die Methode von Idler,[2] um das Begleitsterin möglichst zu erfassen. Die rohen Sterine aus Rotalgen von Nr. 1～9 (Tabelle I) wurden nämlich in *p*-Phenylazobenzoate übergeführt. Bei der Chromatographie dieses *p*-phenylazobenzoates erhielten wir orangefarbene Kristalle vom Schmp. 189°. Sie waren identisch mit Cholesteryl-*p*-phenylazobenzoat[6] und ihre Verseifungsprodukte erwiesen sich nach Vergleich des IR-Spektrum und Acylderivates mit dem authentischen Präparat, reines Cholesterin, ebenfalls identisch. Bei der Reinigung der Sterine aus Braunalgen von Nr. 1～3 (Tabelle II) nach dieser Methode wurde das Fucosterin gewonnen. Man konnte daher in diesen Meeres-algen nicht das Begleitsterin auffinden.

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