

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, UNIVERSITY OF NORTH CAROLINA]

THE IODINE CONTENT OF SHRIMP WASTE

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The recent investigation of Vilbrandt and Abernethy³ on the utilization of the waste products of the shrimp fisheries has shown that a high protein stock feed, rich in vitamins, can be produced economically from the shrimp waste. Since practically all marine life contains comparatively large quantities of iodine, the above wastes from shrimp have been examined for iodine content.

Source of Material.—The shrimp waste used in this investigation was taken from the composite of a number of brine cooks prepared by Vilbrandt and Abernethy³ during the summer of 1928 at Brunswick, Ga. The waste from the shrimp picking tables had been boiled in brine, then removed from the cooking liquor and dried to a moisture content of 4.4%. This material had been kept in this condition for twenty-two months with no indication of deterioration. The methods of Baumann,⁴ Paolini⁵ and McClendon⁶ were used to reduce the shrimp waste to a condition whereby extraction could be accomplished efficiently.

Methods for Determining Iodine.—The analytical method used in this investigation was the Tressler and Wells⁷ modification of the von Fellenberg extraction method. In the case of the extracts prepared and analyzed, one gram of the shrimp waste was used as a base to distribute and support the extract. This procedure added a definite constant amount of iodine to the extraction values; a correction was made for this iodine added.

Experimental Data.—The treatment of the shrimp waste to ascertain the distribution of the iodine was varied by using several solvents and methods of extraction. The extraction data and the iodine content of the various extracts are given in Table I.

Of the various treatments used, simple extraction with ethyl alcohol, water and ethyl ether, in the order named, gave the most efficient separation of iodine. The ether extract contained the lipoid iodine, while the water and alcohol extracts contained considerable quantities of organically combined iodine as well as the inorganic iodine.

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³ F. C. Vilbrandt and R. F. Abernethy, "Utilization of Waste Shrimp," U. S. Bur. of Fisheries, Doc. 1078 (1930).

⁴ Baumann, *Z. physiol. Chem.*, **21**, 319-330 (1895-1896).

⁵ N. Paolini, *Inst. Chim. Pharm., Rome Univ. Mon. Sci.*, **23**, 648 (1894).

⁶ McClendon and others, *THIS JOURNAL*, **52**, 541 (1930).

⁷ O. K. Tressler and A. W. Wells, "Iodine Content of Sea Foods," U. S. Bur. of Fisheries, Doc. 967.

TABLE I
IODINE CONTENT OF EXTRACTS OF SHRIMP WASTE

Treatment	Solvent	Concn., %	Sample, g.	Nature of residue	Iodine in sample, p. p. m.			Iodine, %		Iodine found, %
					Sol.	Insol.	Total	Sol.	Insol.	
1	16.90	100.0
2	Alcohol	96	30	Brown tar	4.68	2.78	7.46	62.7	37.3	44.1
3	Ether	100	30	Greenish brown oil	3.45	5.95	9.40	36.7	63.3	55.6
4	Water	...	60	Brown tar	9.15	7.65	16.80	54.5	45.5	99.4
5	HCl	5	30	Putrid brown mass	..	10.10	10.10	0.0	100.0	60.0
6	NaOH	5	30	Putrid brown mass	8.00	8.94	16.94	47.2	52.8	100.0

The results of the acid hydrolysis indicated that coagulation of protein matter caused by the acid tended to render the iodine compounds insoluble. The alkaline hydrolysis showed that a large fraction of the iodine is held in some organic combination, probably protein, quite resistant to decomposition. It will be noticed that the values for total iodine, obtained by adding the extract iodine and residue iodine, are low in the samples treated with alcohol and with ether. It is possible that some of the loss of iodine is due to volatilization of some organic iodides, possibly ethyl iodide formed with the alcohol itself or the alcohol present in the ether.

These experiments show that the shrimp waste contains a relatively large proportion of iodine. The majority of this iodine is held in organic combination, 26.7% being combined with the lipid material, and the rest probably occurring in protein combination.

Examination for Thyroxine.—An attempt was made to isolate thyroxine from the shrimp waste by means of Kendall's⁸ method of hydrolysis, modified slightly in the extraction procedure due to the peculiar nature of the waste. Upon proper extraction the Kendall precipitate, which should normally contain the thyroxine if any were present, was so small that it was deemed inadvisable to make a direct iodine determination; instead, the substance in solution, slightly yellow in color, was tested for the presence of thyroxine according to the nitrous acid method cited by Kendall,⁸ with negative results. The addition of ammonium hydroxide to the resultant solution also produced no color change, thus indicating that thyroxine could not be detected in the extract of shrimp waste by the Kendall method.

Summary

1. The wastes of shrimp fisheries showed a content of 16.9 parts per million of iodine calculated on the dry basis.
2. Alcohol extraction indicated the presence of 44.14% of organic plus inorganic iodine.

* E. C. Kendall, Thyroxine, American Chemical Society Monograph Series, No. 47.

3. Ether extraction indicated the presence of 55.86% of lipid iodine.
4. No thyroxine could be detected in the extract of shrimp waste when tested by the Kendall method.

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THE REDUCING ACTION AND CONSTITUTION OF THE GRIGNARD REAGENT

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A. Reducing Action

The occurrence in the literature of over fifty references to the reduction of various compounds, chiefly aldehydes, ketones and esters, brought about by Grignard reagents indicates the frequency with which this side reaction is encountered. During the past year alone, from papers and a note have appeared dealing primarily with this subject.¹

An examination of the various experiments leads one to the conclusion that the reduction may be due to a number of causes. It may be brought about by the action of unused magnesium and the magnesium halide which is always present,² by the action of magnesium alcoholate on an excess of the aldehyde or ketone,³ or by the action of the Grignard reagent itself. It would seem that, strictly speaking, only the last type of reduction should be considered as the reducing action of the Grignard reagent, but even in this case reduction may be brought about in at least two ways. Where dissociation of the Grignard reagent into the free hydrocarbon radical and magnesiumous halide may take place, the latter may cause reduction.⁴

In other cases reduction takes place at the expense of the hydrocarbon radical with the formation of unsaturated hydrocarbon.⁵ It should be

¹ (a) Hatt, *J. Chem. Soc.*, 1623 (1929); (b) Conant and Blatt, *THIS JOURNAL*, 51, 1227 (1929); (c) Blicke and Powers, *ibid.*, 51, 3378 (1929); (d) Grignard and Delarue, *Bull. soc. chim.*, [4] 47, 237 (1930); (e) Davies, Dixon and Jones, *J. Chem. Soc.*, 1916 (1930).

² Boyd and Hatt, *ibid.*, 131, 898 (1927) and Ref. 1a; Lagrave, *Ann. chim.*, [10] 8, 369 (1927). See also Gomberg and Bachmann, *THIS JOURNAL*, 49, 236 (1927).

³ Marshall, *J. Chem. Soc.*, 105, 527 (1914); 107, 509 (1915); 127, 2184 (1925); Meisenheimer, *Ann.*, 446, 76 (1926).

⁴ Gilman and Fothergill, *THIS JOURNAL*, 51, 3149 (1929).

⁵ Of the several theories that have been proposed for this last type of reduction, the assumptions (1) that after a primary addition of RMgX to the aldehyde or ketone, unsaturated hydrocarbon is lost and the remaining HMgX adds to the carbonyl group [Hess and Rheinboldt, *Ber.*, 54, 2043 (1921); Hess and Wustrow, *Ann.*, 437, 256 (1924); Rheinboldt and Roleff, *Ber.*, 57, 1921 (1924); Meisenheimer, *Ann.*, 442, 180 (1925); Rheinboldt and Roleff, *J. prakt. Chem.*, 109, 175 (1925)] and (2) that the free radicals $\text{RR}'\text{C}(\text{OMgX})-$ and $\text{R}''-$ are intermediate products in the reaction of a ketone RCOR'