Table V. Miscellaneous Herbicides Screened for Nitrosamine Contamination; Other Pesticides Screened for Nitrosamine Contamination

sample	ingredient	GLC-TEA, ppm	LC-TEA, ppm	LC-UV, ppm	GLC-Hall, ppm
	Miscellaneous Herbicides				
N-19	3,6-dichloro-*o*-anisic acid	neg[b]	*d*		
N-68[a]	diethanolamine salt of 2-*sec*-butyl-4,6-dinitrophenol		233 DELNA[c]	217 DELNA	
N-70	2-*sec*-butyl-4,6-dinitrophenol	neg			
N-81	3-(3,4-dichlorophenyl)-1,1-dimethylurea	neg			
N-86	3-(3,4-dichlorophenyl)-1,1-dimethylurea	neg			
N-88	2-ethoxy-2,3-dihydro-3,3-dimethyl-5-benzofuranyl methanesulfonate	neg			
N-89	same as N-88	neg			
	Other Pesticides				
N-41	bis(dimethylthio)carbamoyl) disulfide	neg			
N-60	diphenylamine	neg			
N-76	sodium [4-(dimethylamino)phenyl]diazene sulfonate	neg			
N-77	same as N-76	neg			
N-84	bis(dimethylthiocarbamoyl) disulfide	neg			
N-7	2,3,5-triiodobenzoic acid	neg			

[a] Presumed to be diethanolamine salt. [b] Less than 1 ppm. [c] Diethanolnitrosamine. [d] A blank indicates that the sample was not analyzed by that method.

used when working with nitrosamines. All trash from the laboratory should be disposed of separately if possible.

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COMMUNICATIONS

Protein Quality Evaluation of Spent Hops

Protein quality of hops, from which the resin had been hexane extracted, was evaluated. Total protein content of the spent hops was 22.43%. A complete amino acid profile of spent hops was determined and evaluated with regard to human requirements. Calculation of a computerized protein efficiency ratio (C-PER) revealed a very low C-PER value (0.11). The low C-PER value was attributed to the low in vitro protein digestibility, 64.52%, as well as the low levels of sulfur amino acids and lysine. By comparing the amino acid profiles of the whole hop plant and spent hops, it was evident that the extraction process significantly reduces the protein efficiency ratio of hop proteins. Feed manufacturers may find the amino acid profile of spent hops useful for formulating rations as it has not been published elsewhere.

Spent hops are a byproduct of the hop-extraction process. U.S. hop production in 1977 totaled 54.8 million pounds. More than 16 million pounds were used for extract production. Only 30% of the hop is extractable as a resin for use in the brewing of beer. Thus, there was in 1977 an excess of 12 million pounds of vegetative discard or spent hops.

Early research of this byproduct was directed toward its use as a feed for sheep (Kellner, 1879; Weiske et al., 1879). Davies and Sullivan (1927) were the first to report animal feeding trials on spent hops in the United States. They observed that spent hops were not eaten readily by sheep and could only be included in a ration in an amount equal to about one-seventh of the dry weight of the total ration. All of these early experiments were conducted with low numbers of sheep that were fed for very limited periods of time. Furthermore, the spent hops used in these early studies were extracted with water rather than with hexane. Nevertheless, the observation that spent hops are not of as high a quality as conventional forages remains accurate.

The use of spent hops as an animal feed was not reported again until 1974, when Heinemann and Dyer conducted feeding studies with cattle. In a steer feeding trial they found that spent hops satisfactorily replaced one-third of the alfalfa cubes. These workers found that spent hops contained approximately 20.6% protein, a relatively high protein content. In an effort to develop a high value byproduct, the quality of the protein for man

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was evaluated in this study. The effect of the extracting process on protein quality also was considered.

MATERIALS AND METHODS

Evaluation of Protein. Spent hops were provided by a commercial hop extraction firm. The hops had been extracted with hexane. The amino acid composition of the spent hops was determined with a Beckman 120C amino acid analyzer after hydrolysis in 6 N HCl at 110 °C for 24 h. The computed protein efficiency ratio (C-PER) was calculated as described by Satterlee et al. (1977). Protein digestibility was determined by the method of Hsu et al. (1977).

RESULTS AND DISCUSSION

Protein content of the spent hop sample was 22.43%, close to the 20.6% reported by Heinemann and Dyer (1974). The amino acid profile of spent hops is compared to that of the whole hop plant in Table I. Relative to the amino acid content of the whole hop plant, the concentration of all amino acids essential to man was reduced.

Table I. Comparison of the Amino Acid Composition of Spent Hops and the Whole Hop Plant

amino acid	grams of aa (100 g of protein)		% of aa relative to whole hop plant
	spent hops	whole hop plant[b]	
alanine	5.16	5.84	88.4
ammonia	3.52		
arginine	11.02	4.32	255.1
aspartic acid	14.21	11.61	122.4
cystine[a]	0.0		
glutamic acid	14.94	12.27	121.8
glycine	4.54	5.38	84.4
histidine	2.09	1.82	114.8
isoleucine[a]	2.98	5.40	55.2
leucine[a]	6.63	8.65	76.6
lysine[a]	3.03	3.82	79.3
methionine[a]	1.02	2.50	40.8
phenylalanine[a]	4.02	5.60	71.8
proline	4.53	4.79	94.6
serine	5.84	4.97	117.5
threonine[a]	3.37	5.26	64.1
tryptophan[a]	1.20		
tyrosine	2.90	3.85	75.3
valine[a]	3.99	5.51	72.4
	90.27	91.59	

[a] Essential amino acids used for calculating the computerized protein efficiency ratio. [b] Stojsavljevic et al. (1976).

Calculation of the computerized protein efficiency ratio of the spent hops using the amino acid profile and in vitro protein digestibility yielded a value of 0.1. Compared to the C-PER value of the whole hop plant, which is 1.49, the C-PER of the spent hops is quite low. For comparison, casein, which is considered a very high quality protein, has a C-PER value of 2.5. The low level of protein in vitro digestibility, 64.52%, accounts in part for the low C-PER value of the spent hops. Relatively low levels of essential amino acids also contribute to the low C-PER value of spent hops. The concentration of sulfur-containing amino acids was relatively low in the spent hops, with methionine and lysine being respectively the first limiting amino acids. The low quantity of lysine could be due to browning losses which occurred during drying (Liener, 1960).

Since the quality of the protein during the extraction of hops is reduced considerably, isolation of the protein from spent hops for human consumption does not seem worthwhile. However, it should be mentioned that isolation of protein from the spent hops would improve protein digestibility and thereby increase the C-PER value.

Careful control of processing parameters during the hop extraction process should be evaluated as to their effect on protein quality. Minimizing protein quality loss during extraction also would improve the protein efficiency ratio of spent hops.

The specific amino acid requirements of many domestic animals are well defined according to the Nutrition Committee on Animal Nutrition of the National Research Council (1977). Although the amino acid composition of the whole hop plant has been published (Stojsavljevic et al., 1976), no reference as to the amino acid composition of spent hops can be found in the literature. Thus, the amino acid composition of spent hops may be useful to feed manufacturers formulating rations for particular animal species. The ruminant most probably could do a much better job of digesting protein from this material than does the nonruminant. Maintaining nutrient balance in animal rations continues to be an opportunity for utilization of food processing byproducts.

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Stanley E. Wallen*
Henry F. Marshall, Jr.
Department of Food Science and Technology
University of Nebraska
Lincoln, Nebraska 68583

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