Amino Acids of Citrus Seed Meal[1]

ABSTRACT

Defatted seed meal from oranges and grapefruit contained more sulfur amino acids but less lysine than some common oilseed proteins. Grapefruit seed meal had less tryptophan and more sulfur amino acids than orange seed meal. Probable annual yields of Florida citrus seed oil, meal and hulls are 17, 23 and 13 million lb, respectively.

A significant amount of research concerning the amino acids of various citrus fruits has been published, with considerable emphasis on the juice fraction of the fruit (1,6,7). To our knowledge, the present paper is the first publication of the amino acid composition of citrus seed meal, a byproduct obtained when processing the seeds for oil (2). The defatted meal is sold commonly as an animal feed supplement, but has a potential for other food uses, e.g., as a clouding agent for beverage bases (3).

The amino acid content of Valencia orange and Duncan grapefruit seed meals is presented in Table I. The values are averages of three analyses each from seed meals (50% protein, 9% moisture) obtained during two different processing seasons. Analyses were accomplished by ion-exchange chromatography using an amino acid autoanalyzer. Hydrolysis times of 24 and 70 hr were used, extrapolating to time, $t = 0$ to obtain the values published in the table. Tryptophan was determined by alkaline hydrolysis and a colorimetric procedure (8). The range of values reported in Table I for tryptophan was 111-136 mg/gN (orange) and 65-91 mg/gN (grapefruit).

The data in Table I indicates few outstanding differences when comparing the amino acid composition of orange and grapefruit seed meals. The amounts of cystine and methionine were ca. 1.5 times higher in the grapefruit than in the orange seed meal, but orange meal had ca. 1.6 times more tryptophan than grapefruit.

Comparisons of citrus seed meal amino acids listed in Table I with soybean show that for five amino acids important in animal nutrition the citrus seed meals have greater amounts of glycine, cystine, methionine and tryptophan (orange), but less than one-half the lysine of soybean. The lysine content is also less than that of cottonseed and peanut flour, two other products useful in animal feeding (5). Except for casein, fish meal and whole egg, the values for total sulfur amino acids of orange and grapefruit seed meal are greater than in protein from many common sources (5). Because of the high values obtained for the sulfur amino acids, these values were checked independently by another laboratory for accuracy (J.R. Brunner, Michigan State University).

Table II presents some theoretical data of the annual yields of seed oil, meal and hulls from Florida citrus seeds. This data was calculated on the basis of the actual number of boxes of each variety processed during the 1970-71 season (151.6 million boxes total), and represents the potential yield of seed oil, meal and hulls only if all available seeds were processed for these products. Table II shows potential yields of 28, 39 and 21 million lb of seed oil, meal and hulls, respectively. Probably no more than 60% of these values could be attained using commercial seed separators now available.

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TABLE I

Amino Acids of Citrus Seed Meal Compared with Soybean Seed

Amino acid	mg Amino acid/g nitrogen in product		
	Orange	Grapefruit	Soybean[a]
Aspartic acid	548	560	731
Threonine	186	181	241
Serine	239	290	320
Glutamic acid	1594	1623	1169
Proline	256	253	343
Glycine	322	272	261
Alanine	231	230	266
Cystine	110	174	83
Valine	307	333	300
Methionine	112	165	79
Isoleucine	219	224	284
Leucine	394	446	486
Tyrosine	168	166	196
Phenylalanine	306	296	309
Lysine	178	175	399
Histidine	128	108	158
Arginine	695	596	452
Tryptophan	125	79	80

[a]Amino acid values from Reference 9.

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TABLE II

Estimated Annual Yield of Dried Florida Citrus Seed Byproducts

Citrus seed	Millions of lb		
	Oil	Meal	Hulls
Oranges			
Early and midseason	18.6	25.6	14.0
Valencia	4.4	6.2	3.4
Temple	0.6	0.8	0.4
Grapefruit			
Duncan	3.8	5.2	2.8
Marsh	0.4	0.4	0.4
Pink	0.2	0.2	0.2
Other			
Tangerines	0.1	0.2	0.1
Tangelos	0.1	0.2	0.1

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Surface Activity of Glycerol Glycoside Palmitates

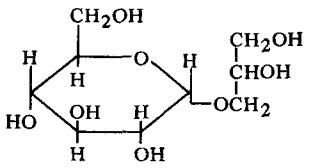
ABSTRACT

A glycoside ester product was prepared by the transglycosylation of starch and glycerol, which yielded a mixture of 2,3-dihydroxypropyl-α-D-glucopyranoside and other glycerol glycosides, followed by interesterification of the crude glycerol glycosides with a mixture of mono-, di- and tripalmitin. The purified reaction product, consisting of ca. 77% glycerol glycoside palmitates, 14% palmitins and 9% free palmitic acid, was found to be extremely effective in lowering the interfacial tension between cottonseed oil and water—a 0.04% concentration in the oil phase lowering the interfacial tension to 1.3 dynes/cm.

Fatty acid esters of the glycerol glycosides occur naturally (1-3), and a patent application has been filed on the use of certain glycoside esters as emulsifiers in foods (4). However reports on the physical properties of such compounds are practically nonexistent. We wish to report on the exceptionally high surface activity found for one type of product.

A number of glycerol glycoside ester products have been prepared and examined by us, but the preparation and characteristics of only one of the products will be reported at this time.

This product, a mixture of glycerol glycoside palmitates, was prepared by a "one pot" procedure. Into a glass reaction flask equipped with a mechanical stirrer there was placed 276.3 g (3.00 moles) anhydrous glycerol and 1.45 g (0.33%, based on the glycerol and starch to be used) of sulfuric acid. The free space in the flask was flooded with nitrogen, the stirrer was started, and the flask and contents were heated to 125 C. While the contents of the flask were kept at 125 C, under nitrogen, and with the stirrer working, 162.14 g (1.00 equivalent of an anhydroglucose unit) of anhydrous, waxy cornstarch was added in the course of 20 min. The reaction was continued for an additional 60 min at 125 C to convert the starch into glycerol glycosides. To this point the procedure is essentially that of Otey et al. (5), which has been shown to yield a mixture of glycosides, including 2,3-dihydroxypropyl-α-D-glucopyranoside,



and its β-anomer.

The reaction flask and its content of glycerol and glycerol glycosides were cooled to ca. 90 C, and 1.564 g sodium carbonate was added slowly to neutralize the sulfuric acid. Sodium palmitate in the amount of 33.10 g (5%, based on the weights of glycerol glycosides, glycerol and the mixed palmitins to be used) was added. Then 223.5 g of mixed palmitins (ca. 60% di-, 22% mono- and 17% tripalmitin) containing 0.75 equivalent of palmitic acid was added.

With the mechanical stirrer working, the head space of the reaction flask again was flooded with nitrogen, and the reactants were heated to and kept at 190 C for 20 min. Glycerol then was removed by vacuum distillation over a period of 80 min, during which time the pressure dropped to 2-3 mm of mercury.

The crude reaction product, a brittle, tan-colored solid, weighed 464.0 g. The product was dispersed in an ethyl acetate-water mixture and washed first with a saline solution containing 0.67 mole orthophosphoric acid per mole of soap, then with a saline solution and finally with water. The glycoside ester fraction, which was found by analysis to be free of soap and unreacted glycosides, amounted to 56.8% of the crude reaction product. Other analytical data on the glycoside ester fraction revealed the properties shown in Table I.

Portions of the glycoside ester fraction were added to cottonseed oil, which had been passed through a silicic acid column to remove any residual soaps; and the interfacial tension of the cottonseed oil solution against water was measured at 70 C with a Cenco-du Nouy interfacial tensiometer. The results are shown in Table II.

The glycoside ester fraction was ca. 130 times more effective than monopalmitin (6) in reducing the interfacial tension between cottonseed oil and water to one-half its original value. Indeed the glycoside ester fraction apparently was even more effective than the ordinary soaps,

TABLE I

Properties of the Glycoside Ester Fraction

Property	Value
Glycoside esters	76.9%
Palmitins	
Mono-	4.2%
Di-	6.1%
Tri-	4.0%
Palmitic acid	8.8%
Hydroxyl value	250
Melting point	59 C

TABLE II

Effect of Glycoside Ester Fraction on Interfacial Tension between Cottonseed Oil and Water

Concentration of glycoside ester fraction in oil, %	Interfacial tension, dynes/cm
0.00	29.4
0.01	14.5
0.02	6.8
0.03	3.7
0.04	1.3