Adsorptive Gossypol Removal[1]

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Gossypol is extractable from cottonseed by using aqueous ethanol. The equilibrium between undissolved gossypol in cottonseed and that dissolved in the solvent determines the residual gossypol. To move the equilibrium toward extraction from the seeds, the dissolved gossypol needs to be removed from the gossypol-solvent-oil mixture. Gossypol removal from the mixture by adsorption on alumina, silica and molecular sieve 5Å was tested. Experimental results indicated that gossypol was more selectively adsorbed than triglycerides by these adsorbents. Alumina and silica had higher gossypol adsorption capacities than molecular sieve 5Å.

KEY WORDS: Adsorption, alumina, cottonseed, equilibrium, ethanol, extraction, gossypol, meal, miscella, silica.

Because of its high nutritional quality, cottonseed has become an indispensable part of food and feed resources. However, cottonseed contains gossypium phenol (gossypol), which is toxic to nonruminants (1). Cottonseed oil and feed are prevalently produced *via* solvent extraction. Depending upon preparatory methods of cottonseed for the solvent extraction, gossypol remains either in a bound or unbound (free) form in the meal. Gossypol is converted to the bound form when heated in the presence of moisture during the seed preparation step (2). Free gossypol left in the meal causes deleterious physiological effects, even to some ruminants (3).

Gossypol can be extracted from cottonseed by using aqueous alcohol (4,5). Because of the gossypol equilibrium between the dissolved and undissolved gossypol, it will be adsorbed back onto the solids of cottonseed flakes, if not removed from the extraction system. This is particularly true when the dissolved gossypol is exposed to areas of the seed matrix where no gossypol is present. To remove the dissolved gossypol by adsorption from the mixture of oil, solvent and gossypol (miscella), silica, alumina and one type of molecular sieve were tested.

MATERIALS AND METHODS

Adsorbents tested were silica, 60–200 mesh (Baker Chemical, Phillipsburg, NJ), neutral alumina, 80–200 mesh, Brockman activity 1 (Fisher Scientific, Fairlawn, NJ), and molecular sieve 5Å, 40–60 mesh (Baker Chemical). These adsorbents were dried in vacuum and packed in glass columns (25 mm i.d. and 30 cm long).

Two types of solutions were used for adsorption tests. The first type of the adsorption test material (solution 1) was prepared by adding pure gossypol (Sigma Chemical, St. Louis, MO) to a miscella mixture produced by extracting cottonseed with 95% aqueous ethanol in a pilot plant extractor (Crown Iron Works, Minneapolis, MN). The details of the miscella preparation have been given elsewhere (6). A second test material (solution 2) was prepared by adding pure gossypol and typical triglycerides of cottonseed (triolein, trilinolein, trilinolenin and palmitodiolein) (Sigma Chemical) to ethanol recovered from the miscella mixture by vacuum distillation. This solution was prepared to simulate the miscella and to exclude phosphatides and polysaccharides.

These two solutions were introduced to the adsorption columns at 25°C under positive nitrogen pressure. The solution volume charged to the column was twice as much as that of the adsorbents. The eluate was collected each minute, but lumped together as long as breakthrough was not observed. Gossypol contents of the eluates were determined by using a high-pressure liquid chromatographic method (7). Triglycerides in the eluate were analyzed in a high-temperature capillary gas chromatographic column (HTCGC) (Chrompac, Raritan, NJ) with the aid of a cold on-column injector (6). Pure gossypol in the simulated miscella (solution 2) and their eluates were also detected by the same capillary gas chromatographic column used for triglyceride analysis.

RESULTS AND DISCUSSION

Figure 1 shows a typical capillary gas chromatogram of the simulated miscella fed to the adsorption column. The first major peak in Figure 1 is gossypol, followed by palmitodiolein, triolein, trilinolein and trilinolenin. A typical HTCGC chromatogram of the eluate from the simulated miscella (solution 2) with neutral alumina is given in Figure 2. Most of the gossypol in the simulated miscella (solution 2) was adsorbed by the alumina in the column. As summarized in Table 1, more than 99% of gossypol charged to the adsorption column was removed. Most of the triglyceride components in the simulated miscella were eluted with the solvent (Fig. 2). This showed that gossypol adsorption by the alumina was highly selective.

Similar results to that shown in Figure 2 also were obtained by the eluate analyses of the silica column. Adsorption capacity of silica for gossypol was as good as that of alumina. However, the chromatographic analyses of eluates from the column packed with molecular sieve 5Å indicated that more than 50% of the gossypol contained in the simulated miscella was eluted along with triglycerides. The gossypol contents in the feed and the eluates are given in Table 1. The cottonseed-derived phosphatides and polysaccharides in the real miscella (solution 1) were expected to compete with gossypol for the available adsorption sites. However, the test results with solution 1 indicated that the presence of phosphatides and polysaccharides did not affect the gossypol adsorption capacities of alumina and silica. The presence of phosphatides and polysaccharides in the real miscella has been reported elsewhere (6,8).

Sorptive removal of some pigments (carotene and chlorophyll) of soy and palm oils by layered minerals, such as montmorillonite, has been investigated (9,10). It was suggested that, along with acid activation, pore size distribution is the dominating variable for the sorption capacity. It also has been reported (11) that zeolite minerals had

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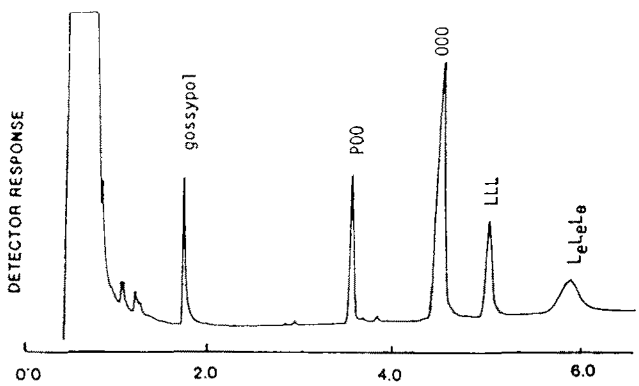

FIG. 1. Capillary chromatogram of simulated miscella.

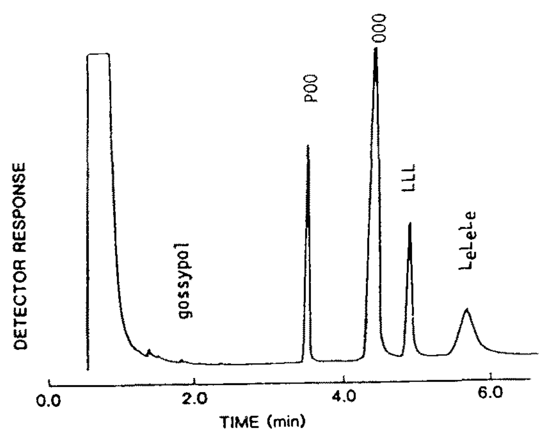

FIG. 2. Capillary chromatogram of alumina eluate.

TABLE 1

High-Pressure Liquid Chromatography Determination[a] of Gossypol in Eluates from Simulated Miscella (solution 1) and Real[b] Miscella (solution 2)

Test solution and eluate type	Gossypol (ppm)
Simulated miscella (solution 1)	750
Alumina eluate from solution 1	1.9
Silica eluate from solution 1	3.2
Molecular sieve 5Å eluate from solution 1	498
Ethanol-rich real miscella (solution 2)	716
Alumina eluate from solution 2	1.3
Silica eluate from solution 2	1.9

[a]These results represent an average of duplicate analyses with a maximum variation of less than ±3% of reported values.
[b]Contained cottonseed-derived phosphatides and polysaccharides.

poor sorption capacity for color components because of the restricted distribution of pore sizes. It is interesting that in the present study the molecular sieve (synthetic zeolite) also had a poor sorption capacity for gossypol. Although the chemical structure and nature of gossypol are quite different from those of carotene or chlorophyll, the pore size distribution may play an important role in this gossypol adsorption. According to Salvaville (12), transition alumina used in this investigation has a broad range of micro- and macropore size distributions, ranging between 10 and 300 Å. Compared to the rigid restriction of the pore size distributions of molecular sieves, alumina and silica were expected to have higher sorption capacities for gossypol because of their broad ranges of accessible pore sizes. Stokes' radii of gossypol and triglycerides (6), with molecular weights near 1000, are in the order of 10–20 Å. Hence, it was not expected that the structured pores of molecular sieves were available to molecules as large as gossypol. In mineral oils, aromatic compounds are known to adsorb more strongly to monolayered earth materials than saturated alkyl compounds. This phenomenon was observed (Fig. 2), indicating high potential for these adsorbents to selectively remove gossypol from extraction solvents.

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