Argan Oil-In-Water Emulsions: Preparation and Stabilization

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ABSTRACT: We prepared stable oil-in-water emulsions of argan oil with two different types of mixtures of nonionic emulsifiers. Three different types of oil (Israeli argan oil, Moroccan argan oil, and soybean oil) were emulsified with mixtures of Span 80 and Tween 80. The optimum HLB value for argan oil was 11.0 (±1.0). The argan oil-in-water emulsions were stable for more than 5 mon at 25°C. Synergistic effects were found in enhancing stability of emulsions prepared with sucrose monostearate. The origin of the oil and the internal content of natural emulsifiers, such as monoglycerides and phospholipids, have a profound influence on its interfacial properties and on the stability of the argan oil-in-water emulsions.

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KEY WORDS: Argan oil, *Argania spinosa* L., edible oil, oil-in-water emulsions, Span 80, stabilization, sugar esters, synergism, Tween 80.

The argan (*Argania spinosa* L.) is a thorny evergreen tree that is native to the semidesert areas of southwestern Morocco. However, it is also grown at two sites in the Negev Desert of Israel, which differ in their environmental conditions.

The tree bears plum-sized fruits that have a stone-like structure and contain one to three kernels with a high oil content. The oil content depends on the genotype and environmental conditions and ranges from 50 to 56% of the kernel (1). It contains 80% unsaturated fatty acids (46–50% oleic acid and about 33–36% linoleic acid) and only small amounts of linolenic acid (0–1%). Its high degree of unsaturation may make it a high-quality oil from a nutritional point of view (1,2). Fatty acid compositions of (Moroccan) argan oil appear in the literature (2–4) and are compared to our results (Table 1, Israeli oil). Argan oil has a high dietetic and culinary value because of its high percentage of unsaturated fatty acids and its rich aroma and flavor. It is used mainly in Morocco as an edible oil, but it also figures in folk medicine and cosmetics. In Israel, argan was examined as a new crop to the Negev Desert (3,5,6).

The unsaponifiable part of argan oil constitutes about 0.8% by weight (4,7). The antioxidant compounds (tocopherols, phenols, and carotenoids) are present in relatively high concentrations and contribute to the preservation of the oil and to its dietetic value (3,4,7). Among the identified sterols, schottenol (5α-stigmasta-7-en-3β-ol) shows an anticarcinogenic effect (4).

Some of the physical and chemical properties of Moroccan argan oil are reported in the literature (3,4) and confirmed by our results (Table 2).

Argan oil is a stable oil because it contains a significant amount of natural antioxidants, mainly tocopherols (3,7,8). In our laboratory, it was realized that oxidation resistance in both Israeli and Moroccan argan oil is greater than in any other commercially available oil (olive, soybean, etc.) (manuscript in preparation).

Owing to its high stability, argan oil may, in certain instances, be a substitute for other oils, such as soybean or corn oil, in preparations of oil-in-water (O/W) or water-in-oil (W/O) food emulsions. The lifetime of emulsions prepared with argan oil may be longer without the need for added synthetic antioxidants. In this paper, a study is reported on the preparation and stabilization of argan O/W emulsions with mixtures of nonionic emulsifiers, such as Tween 80 and Span 80, for possible cosmetics, food, or pharmaceutical applications.

In nonionic surfactant emulsion systems, the stability of a fine emulsion is related to the solubility state of oil and sur-

TABLE 1
Fatty Acid Composition of Israeli and Moroccan Argan Oils

	Range (wt%)	
Fatty acid profile	Israeli oil	Moroccan oil
Myristic (14:0)	0.2	0.2–0.3
Palmitic (16:0)	13–15	12–14
Palmitoleic (16:1)	—	0–1
Stearic (18:0)	2–4	5–7
Oleic (18:1)	46–55	42–47
Linoleic (18:2)	28–35	31–37
Linolenic (18:3)	0–0.5	0–1
Arachidic (20:0)	0–0.3	0–1
Gadoleic (20:1)	—	Trace
Behenic (22:0)	0	Trace
TUFA/TSFA[a]	4.93	4.29

[a]TUFA, total unsaturated fatty acids (oleic + linoleic); TSFA, total saturated fatty acids (palmitic + stearic).

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TABLE 2
Some of Physical and Chemicals Properties of Israeli And Moroccan Argan Oils

	Israeli oil	Moroccan oil
Refractive index (20°C)	1.47	1.46–1.47
Relative density	0.90–0.92	0.91–0.92
Saponification value	189–195	189–195
Acid value	2.0–2.8	1.3–3.0
Peroxide value (meq O_2/kg)	0	<3
Unsaponifiable (%)	0.6–0.9	0.3–1.1
Iodine value	95–100	92–102

factant (9). Chow and Ho (10) reported that the difference in behavior between palm O/W emulsion and other emulsions, prepared with aliphatic hydrocarbons as the oil phase, can perhaps be traced to the fact that the palm oil contained a small amount of natural surface-active materials, such as monoglycerides and phospholipids, which can have a profound influence on interfacial properties of the palm oil/water interface.

It is the aim of this paper to determine the optimum required hydrophile–lipophile balance (HLB) value for argan oil, to establish the appropriate emulsification technique that will give a stable argan O/W emulsion, and to compare the stability of these emulsions with emulsions of different types of oil.

MATERIALS AND METHODS

Materials. The oils and surfactants were used without further purification. Medium-chain triglycerides (MCT), isopropyl myristate (IPM), and tricaprylin were supplied by Sigma Chemical Co. (St. Louis, MO). Soybean oil was purchased locally. Samples of Israeli argan oil for this study were prepared in the laboratory. Kernels of argan were mechanically crushed, and the oil was obtained by cold pressing. Moroccan argan was purchased in Morocco. The emulsifiers Span 80 (sorbitan ester of oleic acid) and Tween 80 (ethoxylated-20 EO-sorbitan monooleate) were of commercial grade and purchased from Sigma. Sucrose monostearate (S-1570, HLB 15) was obtained from Mitsubishi-Kasei Food Corp. (Tokyo, Japan). The water was deionized.

Preparation of the emulsions. Span 80 (the oil-soluble emulsifier) was always dissolved in the oil phase, and Tween 80 (the water-soluble emulsifier) in the aqueous phase. The oil was added dropwise to the continuous phase, followed by homogenization for 15 min (Ultra Turrax model T25, Janke & Kunkel GmbH, Staufen, Germany).

In some samples, the emulsions were further sheared in a Microfluidizer (model TC-110; Microfluidics Corp., Newton, MA).

Size of the emulsion droplets was determined under a light microscope (Nikon AFX-IIA, equipped with a Nikon FX35W camera, Japan) and measured (for up to 30 d) by a Coulter counter (model TA-II; Coulter Electronics, Luton, United Kingdom) and/or a Galai Computerized Inspection System (Galai, model CIS-1, Migdal Haemek, Israel).

Emulsion stability was determined by measuring spectral absorption of a given diluted emulsion at room temperature at two wavelengths (400 and 800 nm) and obtaining a stability index ($R = Abs_{800}/Abs_{400}$) (11,12), and by measuring the separation of oil (wt%) from emulsions stored in a water bath at 50°C as a function of time. The emulsion stability decreases with an increase in the value of the stability index.

RESULTS AND DISCUSSION

Required HLB of argan oil. Three series of emulsions, consisting of three different types of oil (Israeli argan oil, Moroccan argan oil, and soybean oil), were examined to find the required HLB to best stabilize the emulsions. All emulsions with 10 wt% oil and 6 wt% emulsifier (mixture of Tween 80 and Span 80) were prepared by homogenization at 9500 rpm for 15 min. The effects of the emulsifiers' HLB on average droplet size (µm) and oil separation (wt%) are shown in Figure 1.

As can be seen from the average droplet sizes and oil separation (which are consistent and show good correlation), the required HLB of soybean oil was 10, whereas the required HLB of argan oil was 11. We also found that the stability fell rather sharply on either side of the required HLB. All emulsions prepared at HLB values below the best required HLB

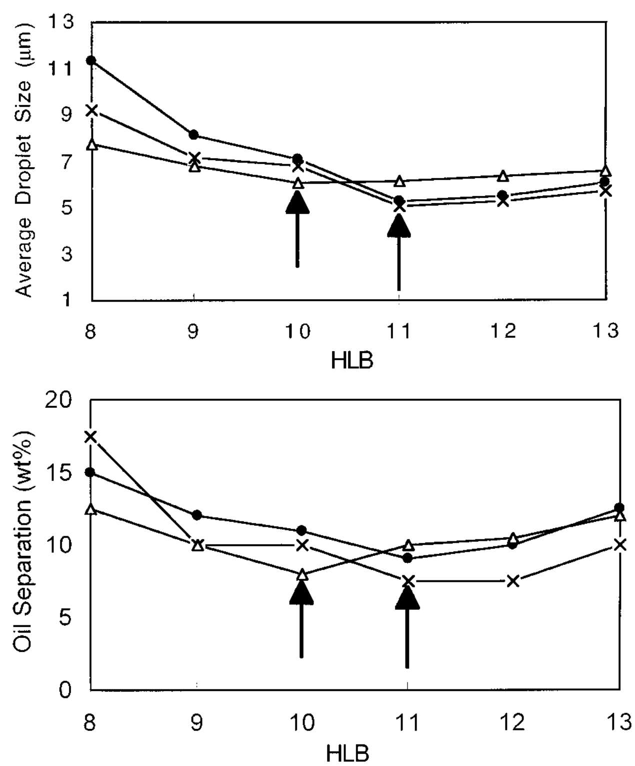

FIG. 1. (A) Average droplet size (µm) and (B) separation of oil (wt%) as a function of HLB for oil-in-water (O/W) emulsions prepared with 10 wt% oil, with various blends of 6 wt% emulsifier (Span 80 + Tween 80). Homogenizer speed 9500 rpm, 15 min. Tests carried out after incubation at 25°C for 1 mon. ●, Moroccan argan oil; ✖, Israeli argan oil; △, soybean oil; ↑, indicates the optimum HLB for the O/W emulsions.

were less stable and had relatively larger average droplet size (μm) and significant oil separation after 1 mon of incubation.

All emulsions prepared at the best-required HLB creamed after storage of 12 d but were stable to coalescence for more than 5 mon at 25°C.

Homogenization time and speed. For some food emulsions, the minimum requirement is no coalescence and flocculation after 1 mon of incubation at room temperature. The homogenizing time and speed have to be set to at least 15 min and 9500 rpm to achieve these requirements. There is no need to increase speed or homogenization time because their effects are minor.

Emulsifier concentration. The influence of emulsifier concentrations on average droplet size and oil separation after a month of aging is shown in Figure 2. Average droplet size and oil separation decreased as emulsifier concentration was increased. The optimal concentration of emulsifier for a stable argan O/W emulsion was 6–8 wt%. Viscosity of the emulsion increased with an increase in emulsifier concentration (10,11). This effect has often been explained as being the result of increased emulsifier adsorption around the surface of a droplet.

Oil phase content. The effect of the oil fraction on Israeli argan O/W emulsion stability was examined at HLB 11.5. Stability index and average droplet size of each emulsion were determined after 1 and 30 d of aging at room temperature. There is a nonlinear increase in stability index (meaning less stability) with increasing amount of oil phase (Fig. 3). At up to $\varphi = 0.15$ (φ is the oil fraction), the loss in stability (increase in stability index) is moderate, and a sharp increase in the stability index (decrease in stability) is observed at $\varphi >$ 0.15.

The average droplet size and the percentage of oil separation after 1 mon of incubation confirm these findings. The most stable emulsions prepared were at $\varphi < 0.1$. An increase in the oil fraction ($\varphi > 0.15$) had a strong negative effect on the average droplet size as a result on emulsion stability.

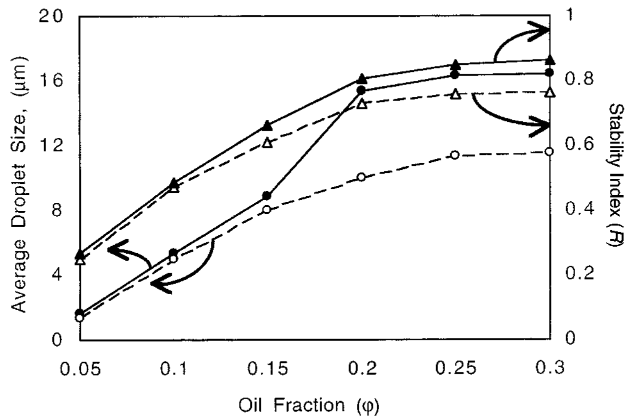

FIG. 3. Effect of weight fraction (φ = 0.05–0.3) of Israeli argan oil on the average droplet size (μm) and stability index (*R*) of O/W emulsions prepared with 6 wt% emulsifier (Span 80 + Tween 80, HLB 11.5). Homogenizer speed 9500 rpm, 15 min). △, stability index (*R*) after 1 d; ○, average droplet size after 1 d; ▲, Stability index (*R*) after 30 d; ●, average droplet size after 30 d. See Figure 1 for abbreviation.

Type of emulsifier. Two series of emulsions that consisted of two different types of emulsifiers were studied. Figure 4 is a summary of the results obtained from emulsions prepared with Israeli argan oil and these emulsifier blends: (i) Tween 80 and Span 80 and (ii) sucrose monostearate and Span 80 (HLB 11.5).

Figure 4 shows that the average droplet sizes of emulsions prepared from the blend of sucrose monostearate and Span 80 were smaller than those prepared from the blend of Tween 80 and Span 80.

No changes were observed in average droplet sizes of these two series of emulsions after 30 d of incubation.

We concluded that there is a synergistic effect in enhancing stability of argan O/W emulsions prepared with sucrose monostearate.

Type of oil. Four series of emulsions that contained different types of oil were examined. The results are shown in Figure 5. It is clear again that the method of emulsion preparation has a significant influence on emulsion stability.

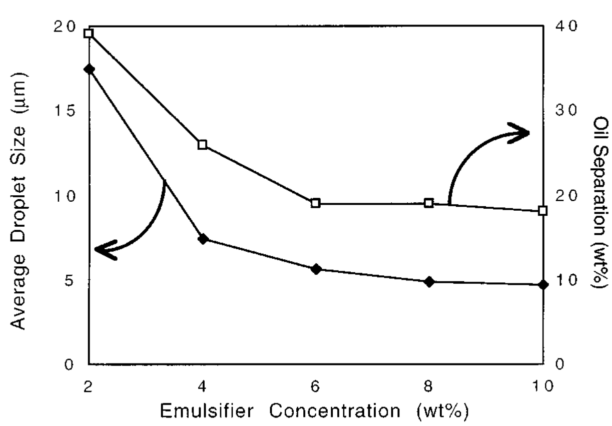

FIG. 2. Effect of emulsifier (Span 80 + Tween 80, HLB 11.5) concentration on average droplet size (μm) and oil separation (wt%) for O/W emulsions prepared with 10 wt% Israeli argan oil. Homogenizer speed 9500 rpm, 15 min. Tests carried out after incubation for 1 mon. ◆, Average droplet size; □, oil separation (wt%). See Figure 1 for abbreviation.

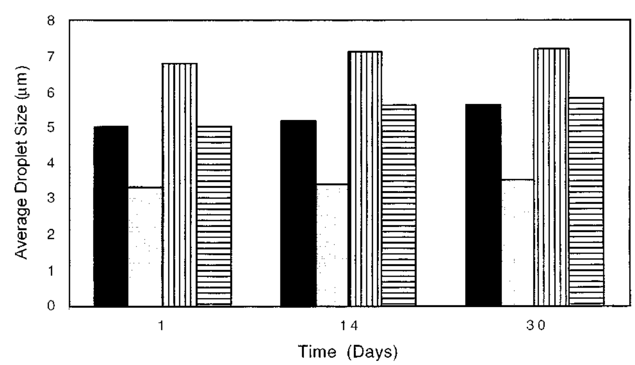

FIG. 4. Effect of mixtures of emulsifier on average droplet size (μm) of argan O/W emulsions prepared with 10 wt% Israeli argan oil, 6 wt% emulsifier. Homogenizer speed 9500 rpm, 15 min. ■, Span 20 + sugar ester, HLB = 10; □, Span 20 + sugar ester, HLB = 11.5; □, Span 80 + Tween 80, HLB = 10; □, Span 80 + Tween 80, HLB = 11.5. See Figure 1 for abbreviation.

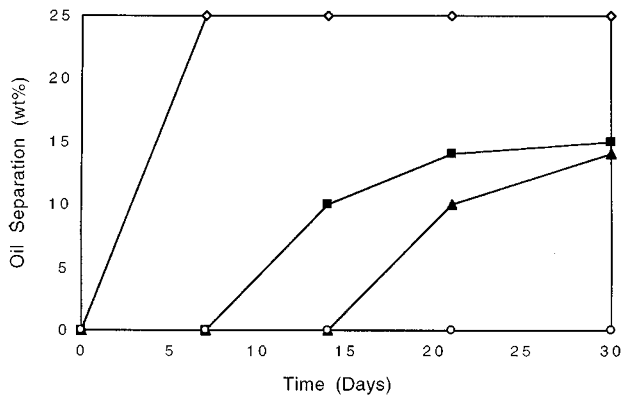

FIG. 5. Effect of oil type on the wt% separation of oil in O/W emulsions prepared with 10 wt% oil, 6 wt% mixture of emulsifiers (Span 80 + Tween 80, HLB 11.5). Homogenizer speed 9500 rpm, 3 min, and 1.5 min in the Microfluidizer. ◇, Soybean oil; ■, Israeli argan oil; ▲, isopropyl myristate; ○, medium-chain triglycerides. See Figure 1 for abbreviation.

The percentage of separation in emulsions prepared with the Microfluidizer was lower than in those prepared with the mechanical homogenizer. The average droplet size of an argan O/W emulsion was 8 μm after homogenization for 3 min, and was reduced to 0.85 μm after the emulsion was passed through the Microfluidizer. No significant changes in average droplet size and stability index were observed, even after 30 d of aging. The emulsions prepared with Israeli argan oil performed better than other O/W emulsions in their stability and droplet size distribution. We assume that the excess stability is related to the existence of relatively high contents of amphiphilic molecules, such as monoglycerides (0.27–0.65 wt%), diglycerides (0.68–1.53 wt%), and phospholipids, which have a profound influence on the properties of the oil/water interface (4,10). These natural emulsifiers have been removed in part by the warm water extraction process (which swells and extracts the polar lipids) employed in Morocco.

The nature of the oil affects the ease of emulsion formation (9,10,13). The difference in stability of argan O/W emulsion and the emulsions that were prepared with IPM or MCT can be attributed mainly to the solubility of Span 80 in the different oils (10). The solubility of Span 80 in argan oil was higher than that of IPM and MCT. Chow and Ho (10), who studied the stability of palm O/W emulsions prepared with mixtures of Tween 40 and Span 40, reported that stable emulsions might be prepared with Tween 40 alone, and that the addition of Span 40 to the oil did not appear to confer any synergistic advantage. The authors deduced that it was likely that Span 40 was not exerting much influence at the oil/water interface because of its good solubility in palm oil.

MCT formed the most stable emulsion: it was stable for more than 7 mon at 25°C and for more than 1 mon at 50°C.

The stability of soybean O/W emulsion was the lowest because it was prepared at an HLB higher than the best required HLB of soybean oil.

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