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SUNSCREEN FORMULATION: A STUDY OF SILICONE-EMULSIFIANT CONCENTRATION

V. Gallardo*, N. Aybar*, A. Hernández* and Ma A. Ruiz*
*Dpto Farmacia y Tecnología Farmacéutica. Facultad de Farmacia. Universidad de Granada.

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Synopsis

Silicone surfactants can be used to prepare emulsions at room temperature, and yiels stable W/O and O/W emulsions with excellent appearance and optimum hydrating and protective properties. Silicones impart substantiveness to the preparation. This was confirmed experimentally in washing-off tests. After 24 h of testing, an acceptable percentage of the initial concentration of sunscreen remained present in the formulation.
Physical stability assays (centrifugation and aging at 25°C, 40°C and 60°C) yielded similar results. Rheological assays, tests at different pH values, and droplet size studies were also done. Stability of the preparations was adequate, pH showed minimal variations, and droplets remained small and homogeneous.

Riassunto

I tensioattivi al silicone possono essere utilizzati per preparare emulsioni a temperatura ambiente ed emulsioni A/O e O/A dall'aspetto eccellente ed ottime proprietà idratanti e protettive. I siliconi conferiscono consistenza alla preparazione. Questo è stato confermato sperimentalmente nei test di washing-off. Dopo 24 ore di test una percentuale accettabile della concentrazione iniziale dello schermo solare rimaneva presente nella formulazione.
Le analisi sulla stabilità fisica (centrifuga e invecchiamento a 25°C, 40°C e 60°C) hanno dato simili risultati. Sono stati altresì eseguite analisi reologiche, test a diversi valori di pH, e studi sulle dimensioni delle gocce.
La stabilità dei preparati era adeguata, il pH ha indicato variazioni minime e le gocce sono rimaste piccole e omogenee.

INTRODUCTION

Advances in silicone chemistry have led in recent years to the development of a wide variety of compounds derived from the basic structure of siloxane bond polymers (1-3).

One type of new compounds are the silicone surfactants with groups of ethylene oxide (EO), propylene oxide (PO) or copolymers of both (EO/PO). W/O and O/W surfactants are defined according to the proportions of EO or PO they contain (4). The advantages of silicone emulsions are that they can be prepared at room temperature, they have adequate extensibility, and do not leave a greasy, sticky, or unctuous film on the skin. These emulsions contain approximately 80% water and are thus of the greatest interest economically (5). The present study on sunscreen formulation was designed with different concentrations of W/O (DC 3225-C) silicone surfactant. The emulsion is prepared at room temperature, the formulae contain almost no greasy or oily components, which imparts the best dry emollient characteristics, and hydratant properties with a photoprotector type screen (titanium dioxide) to be used by people needing total protection from solar radiation, particularly children, people with alipic skin, etc. (6-7).

Physical stability assays of the preparation were made at 25°, 40° and 60°C, and resistance to centrifugation was also used to test stability (8,9).

MATERIALS AND METHODS

- Tioveil AQN (titanium dioxide in aqueous dispersion), supplied by Comercial Quimica Massó (Barcelona) is an oily sunscreen.
- DC 3225-C (a mixture of cyclometione and copolyol dimethicone), a W/O surfactant, and DC-344 (tetrameric cyclomethicone) were supplied by Dow Corning.
- Isopropyl myristate, glycerin and sodium chloride was obtained from Panreac.
- Distilled water was used in all formulations.

Composition of Formulations

The formulation tested is:

	A	B	C
Tioveil AQN	5	5	5
DC3225-C	3	5	8
DC-344	5	5	5
Isopropyl myristate	12	12	12
Glycerin	3	3	3
Sodium Chloride	1	1	1
Distilled water		c.s. 100	

PREPARATION OF THE EMULSION

The galenical formula was developed in accordance with recent technology for preparing emulsions at room temperature.

1. Mix oily components and aqueous components separately.
2. Add the aqueous phase to the oily phase very slowly with rapid shaking at 1700 rpm (ultra-Turrax, T25 IKA labortechnik) under a vacuum if possible, until a milky, homogeneous emulsion forms.
3. Homogeneize in a colloid mill (Lancor-Himmel, 2G.80 1.1.H Bilbao, Spain).

RESULTS AND DISCUSSION

Spectrophotometric Analysis

Fig. 1 illustrates the UV absorption spectra of Tioveil AQN. There is no pronounced peak absorption, indicating the tioveil to be a sunscreen with a protective effect across the entire ultraviolet range, with a slight increase at 375 nm.

Similar effects are obtained with our formulations

(Figs. 1 A,B, and C) which showed the most absorbance for formulation C (the higehest surfactant concentration).

Wash-off Tests

Since the formulations were designed as sunscreens, it was necessary to ensure that the emulsion provided adequate substantiveness.

For 24h, samples were subjected to a water flow at 25°C. The percentage of sunscreen released from the sample is shown in Fig. 2 for different periods. The values are obtained at 375 nm wavelength, where the tioveil showed a slight peak.

After 24 h (i.e. much longer than under conditions of normal use), a maximum of approximately 2-8 % of tioveil had been lost from the formulation. This result indicates that a significant proportion of the filter remains on the skin even after repeated bathing, making it without doubt a highly water-resistant formulation.

The formulation with the least surfactant (A) (the most fluid) showed the most liberation of tioveil, probably due to the low viscosity of the formulation.

Stability Analysis

Since the preparations were thermodynamically unstable, we investigated viscosity and droplet size as well as the organoleptic characteristics of the formulations.

Tests were run at different temperatures in accordance with bibliographic references. Samples were kept at room temperature (25°C) for over six months, at 40°C for 3 months, and at 60°C for two weeks. We then measured pH to check for variations over time, finding the pH values to remain near 7±0.5 for most of the experimental period. Variations in temperature and over time were minimal, indicating that the preparations are stable.

A series of rheological tests was done with samples at room temperature, at 40° C and at 60° C. Fig. 3 shows rheograms for the beginning of the study and Fig. 4-6 shows rheograms for samples followed for six months at room temperature, 3 months at 40°C and two weeks at 60°C, for formulation A,

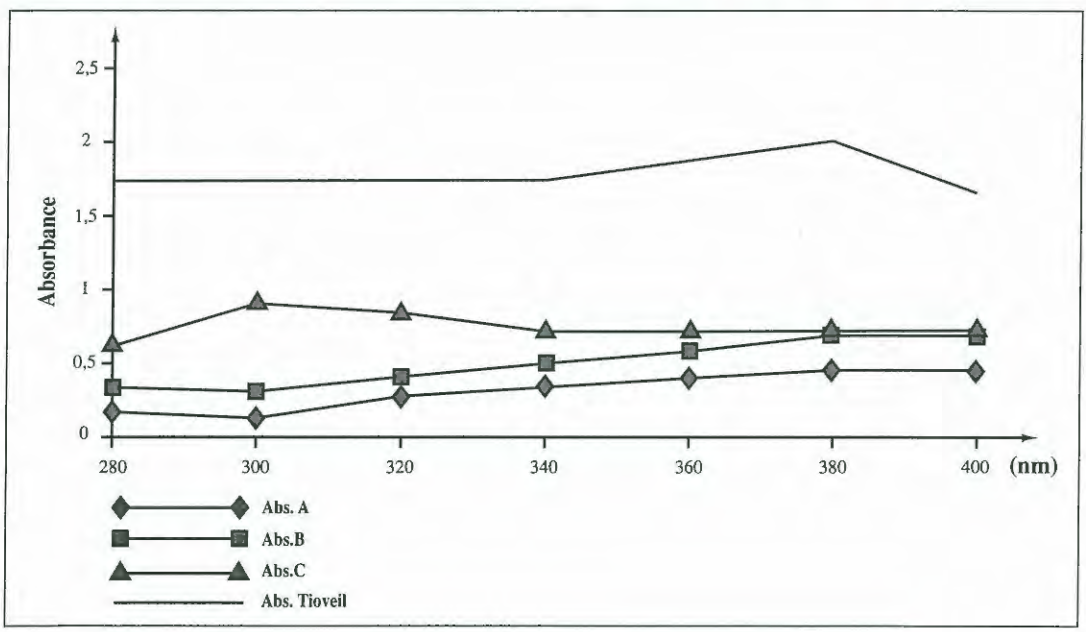

Fig. 1. Absorption spectra of Tioveil AQN and formulations A, B and C.

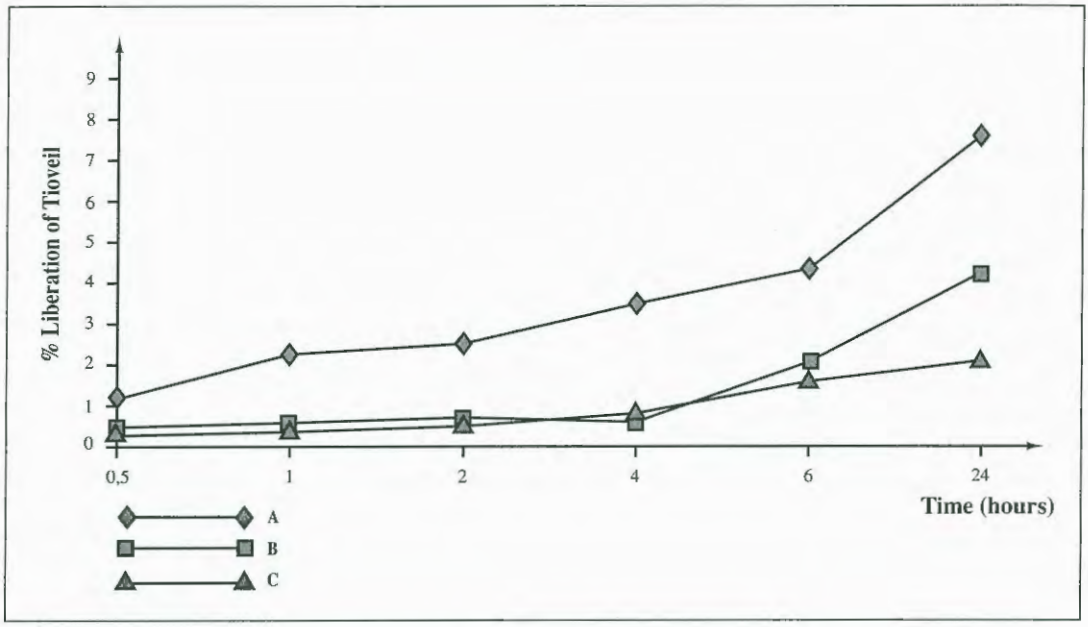

Fig. 2. Percentage of Tioveil AQN released by the formulations A, B and C as a function of time.

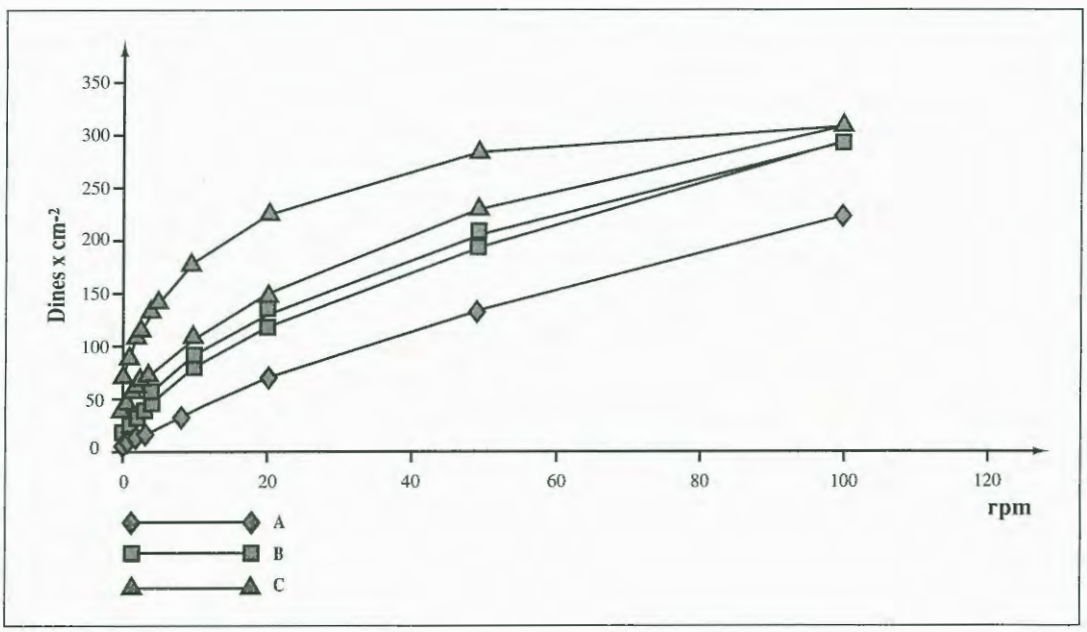

Fig. 3. Rheograms of the formulations A, B and C.

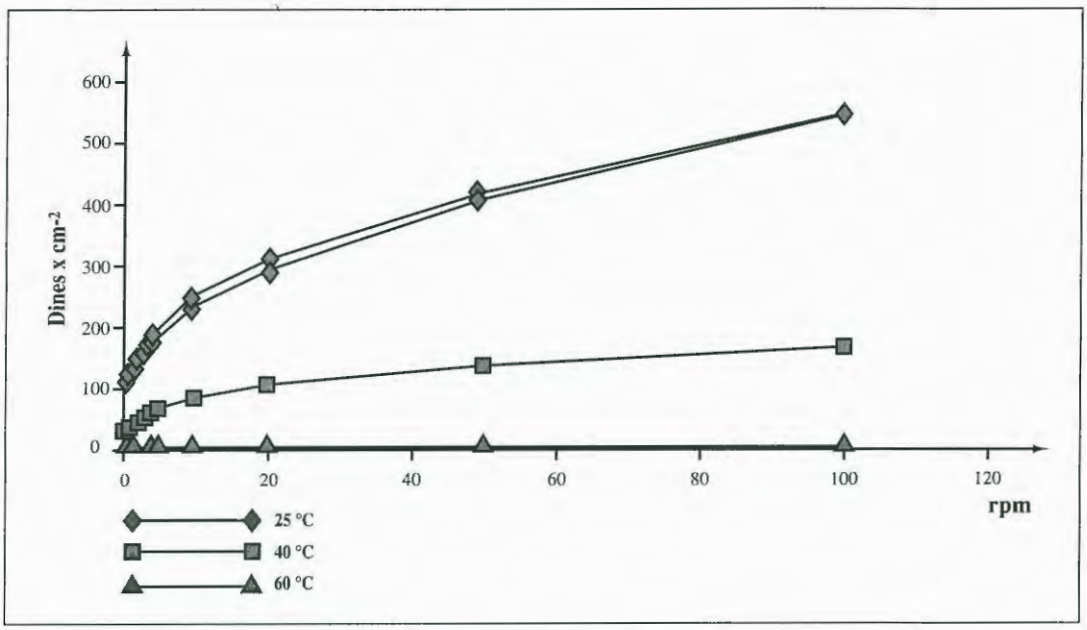

Fig. 4. Rheograms of the formulation A at room temperature 400C and 600C.

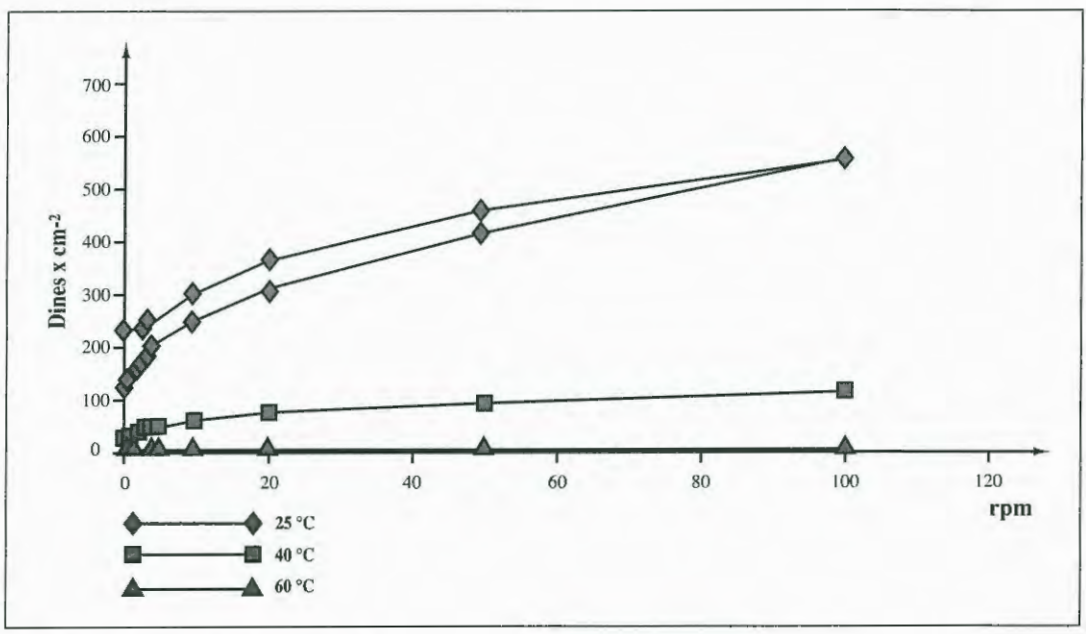

Fig. 5. Same as Figure 4 at formulation B.

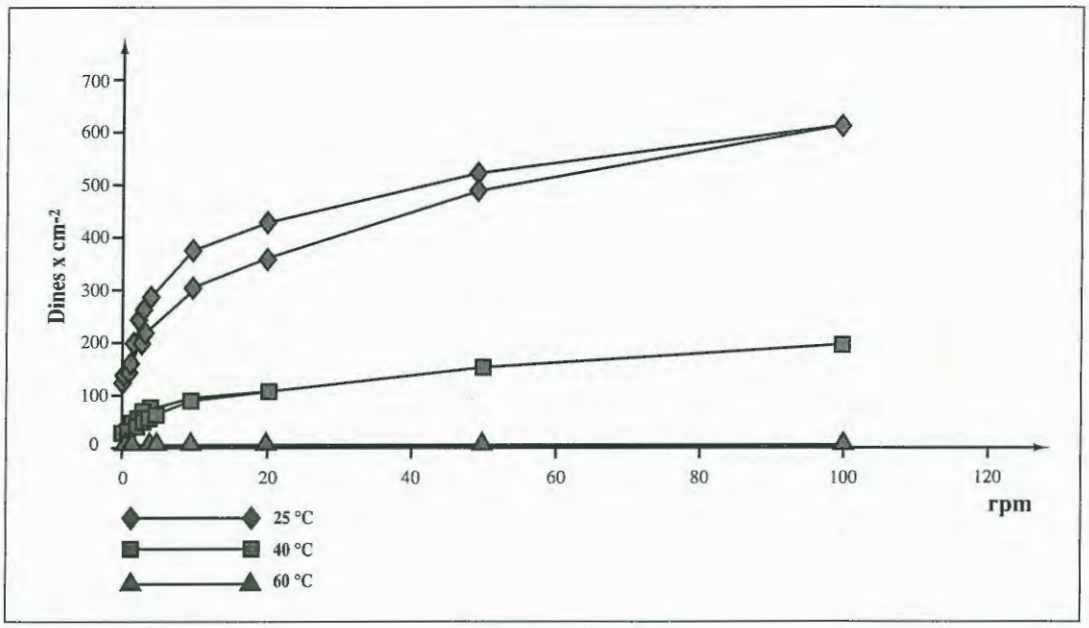

Fig. 6. Same as Figure 4 at formulation C.

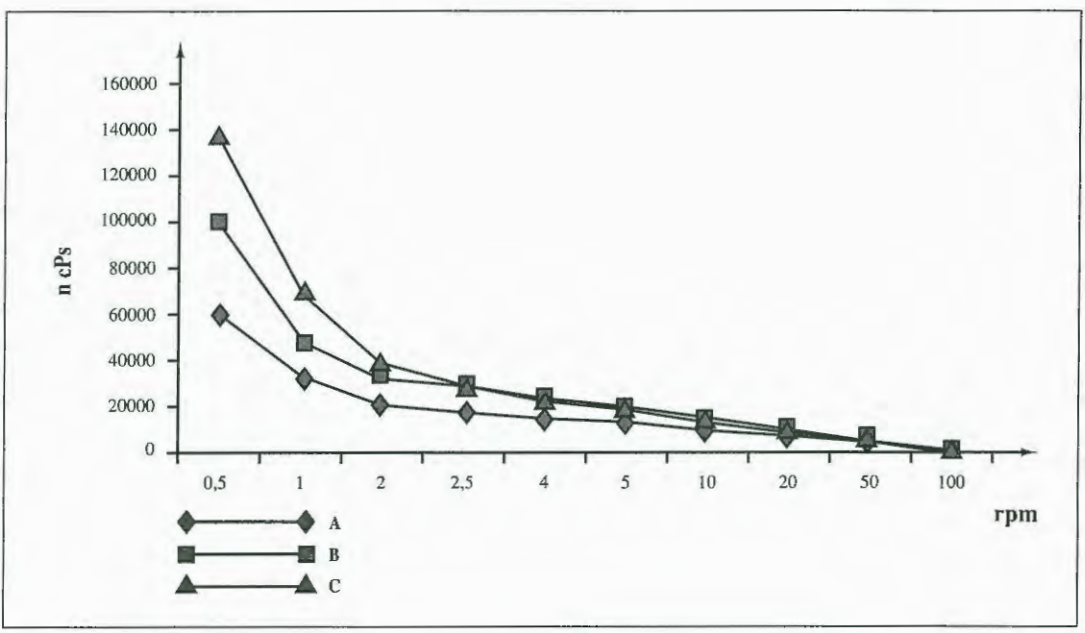

Fig. 7. Changes in viscosity with shear rate in formulations A, B and C.

B and C respectively.
The room temperature rheograms for the three formulations were similar, showing the plastic behaviour characteristic of these preparations. Note the higest deformation force in formulation C. A hysteresis cycle was most prominent in samples with the most surfactant.
The viscosity values showed an increase in surfactant concentration, notable at low shear rate, with nearly identical values from 10-100 rpm (Fig. 7).
These results were verified experimentally with microscopic examination that confirmed the stability of the samples, particularly of sample C (the most concentrated surfactant).
Droplet size remained small and homogeneous, although during the final days of experiment samples at 60°C showed a slight reduction in particle size, with a slight loss of homogeneity in comparison with the beginning of the experiment.
Scarce coalescence was also observed in this samples. Figures 8 and 9 show droplets from sample A that were kept at room temperature (photo 8) for 6 months and at 60°C (photo 9) for two weeks. Resistance to centrifugation was also used to test stability.
This procedure is useful for comparing formulas of similar composition and density on the basis of phase separation, creaming, or exudation. In accordance with bibliographic references, samples were centrifuged at 3000 rpm for 30 min.
None of the tests caused separation of the components in the three formulations, confirming once again the stability of the preparations.

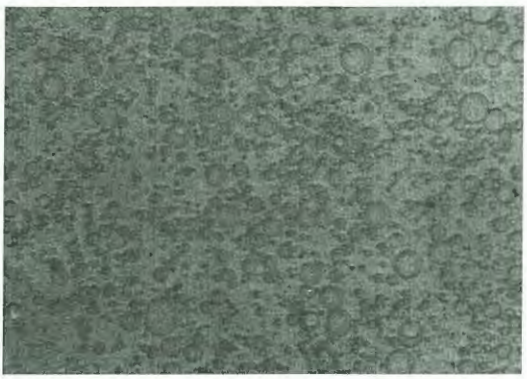

Fig. 8. Optical micrograph of the formulation A at room temperature.

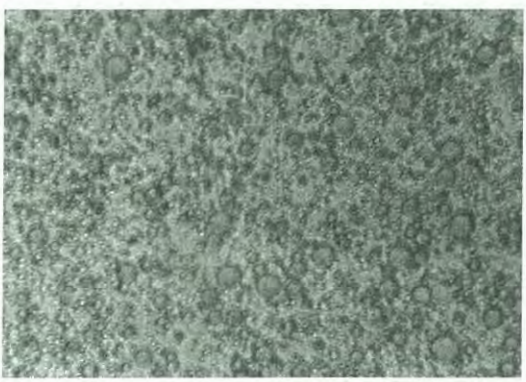

Fig. 9. Same as Figure 8 at 60°C.

CONCLUSION

Of the three formulations studied, all were stable during the time of experiment.
Nevertheless, it is apparent that formulation C has the best organoleptic characteristics, the best substantiveness and the best viscosity, with adequate extensibility.

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Author Address:

V. Gallardo
Dpto Farmacia y Tecnologia Farmaceutica
Facultad de Farmacia
Campus de Cartuja s/n
18071 Granada
Spain
Tel: 0034-95-8243900
Fax: 0034-95-8248958