

THE RELATIONSHIP OF ESTERS AND FREE FATTY ACIDS IN THE SKIN SURFACE LIPIDS IN PERSONS WITH SOME DERMATOSES

An Infra Red Spectroscopic Study

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Abstract. The skin surface lipids were obtained by Enderlin & Brun's method in cases of some dermatoses and in persons without dermatoses. The quantity of lipids has been determined gravimetrically, and infra red spectroscopy of these performed. The significance of some absorption maxima was determined. The spectra of these lipids in cases of dermatoses and those of persons without dermatoses do not differ with regard to the absorption maxima. These maxima were found at constant wavelength. The authors paid attention to the relationships, of the maxima of the esters and free fatty acids in cases of ichthyosis vulgaris, psoriasis vulgaris, acne vulgaris, and persons without dermatoses. This relation probably depends on the activity of esterases in the upper parts of the follicular ducts and the skin surface, as well as on the presence of microorganisms on the skin surface.

Since 1965 we have been studying the infra red spectroscopy of the skin surface lipids in persons without dermatoses and in those with some dermatoses (4, 5, 6). These lipids were obtained by the method of Enderlin & Brun (1) and stored at -4°C until infra red spectroscopic analysis. Spectroscopy was done with the infra red spectroscopy of Perkin-Elmer M 221 or the Perkin-Elmer Infracord TM 137, on samples in solution at pure tetrachlormethane or after evaporation of this solvent. In these studies the significance of some absorption maxima of the infra red spectra of the skin surface lipids was determined.

The maxima were found at constant wavelength. Thus, for instance, the maxima of esters was found between 1750 and 1730 cm^{-1} , that of free fatty acids between 1718 and 1695 cm^{-1} , the first being determined by stretching vibration of the $\text{C}=\text{O}$ group of saturated and unsaturated

esters of fatty acids, the second by stretching vibration of $\text{C}=\text{O}$ group of saturated and unsaturated aliphatic free fatty acids. Furthermore, the three maxima between 1250 and 1100 cm^{-1} signify the presence of triglycerids in the analysed substance. They are determined by stretching vibration of the $\text{C}=\text{O}$ group of triglycerids. The intensity of these maxima always parallels the intensity of the maxima of triglycerids between 1750 and 1730 cm^{-1} (4).

We found further that the infra red spectra of the skin surface lipids of persons without dermatoses and those with some dermatoses, do not differ essentially with regard to the absorption maxima.

In this study we paid special attention to the relation of the absorption maxima of the esters at about 1750 cm^{-1} and free fatty acids at about 1715 cm^{-1} in persons without dermatoses and those with psoriasis vulgaris, ichthyosis vulgaris and acne vulgaris. It must, however, be pointed out that this relationship in the skin surface lipids of a certain individual is not constant (4, 6), in contrast to the opinion of Rothman (3) and Freinkel et al. (2).

In this study the above-mentioned relationship concerns the maxima of esters and free fatty acids in the spectra of lipids obtained at the moment of arrival of the patients at the clinic.

With regard to the relationships of these maxima there are three possibilities:

1. The absorption maximum of the esters can be more intensive than that of the free fatty acids (Fig. 1).

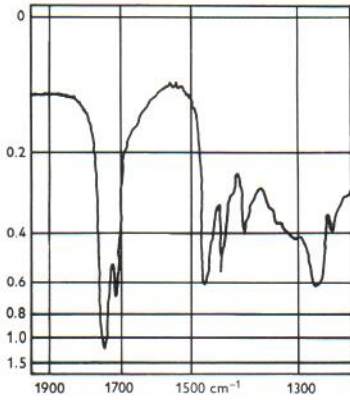


Fig. 1. The absorption maximum of the infra-red spectrum of the esters is more intensive than that of the free fatty acids. Spectrogram made with Perkin-Elmer M 221 in a person without dermatoses.

2. These maxima can be of equal or of approximately equal intensity (Fig. 2).

3. The absorption maximum of free fatty acids can be more intensive than the maximum of esters (Figs. 3 and 4).

RESULTS OF INVESTIGATIONS

A. In the infra red spectra of skin surface lipids of 16 persons without dermatoses, the absorption maximum of the esters was, in 10 cases, more intensive than the maximum of free fatty acids; in 2 cases these maxima were of equal or of approximately equal intensity; in 4 cases the maximum of free fatty acids was more intensive.

B. In the infra red spectra of skin surface lipids of 27 psoriatics, the absorption maximum of the free fatty acids was, in 7 cases, more intensive

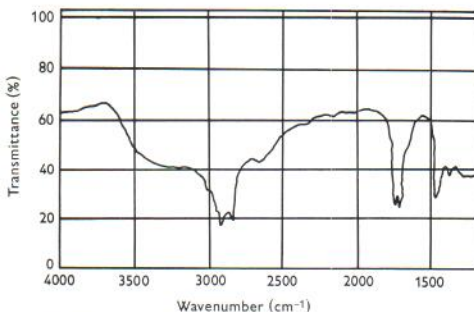


Fig. 2. The absorption maxima of the infra-red spectrum of the esters and free fatty acids are of equal or of approximately equal intensity. Spectrogram made with Perkin-Elmer Infracord TM 137 in a psoriatic.

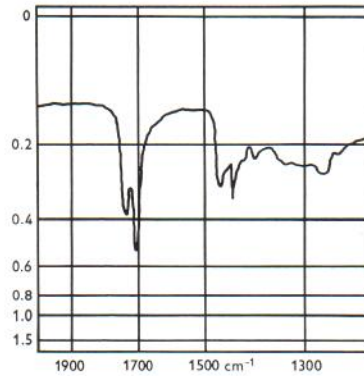


Fig. 3

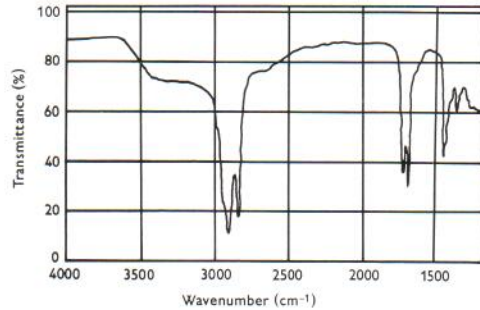


Fig. 4

Figs. 3 and 4. The absorption maximum of free fatty acids is more intensive than the maximum of esters. Fig. 3: Spectrogram made with Perkin-Elmer M 221 in a psoriatic. Fig. 4: Spectrogram made with Perkin-Elmer Infracord TM 137 in a case of ichthyosis vulgaris.

than the maximum of esters; in 6 cases these maxima were of equal or of approximately equal intensity; in 14 cases the maximum of esters was more intensive.

C. In the infra red spectra of skin surface lipids of 25 patients with acne vulgaris, the absorption maximum of the free fatty acids was in only 3 cases more intensive than that of esters; in 6 cases these maxima were of equal or of approximately equal intensity; in 16 cases the maximum of esters was more intensive.

D. In all 4 cases of ichthyosis vulgaris, the maximum of the free fatty acids in the infra red spectra of skin surface lipids was more intensive than the maximum of esters.

DISCUSSION

The quantity of free fatty acids in the skin surface lipids depends mainly on the activity of es-

terases in the follicular ducts and on the skin surface, as well as on the presence of microorganisms on the skin surface (3). In the case of intensive activity of esterases, the quantity of free fatty acids in the lipids of the skin surface will be greater and vice versa.

It is obvious that the intensity of absorption maximum of free fatty acids in the infra red spectrum of lipids from the skin surface, parallels the absolute quantity of those substances in the skin surface lipids. The same is true for the maximum of esters.

From our investigations it follows that the activity of esterases on the skin surface is more intensive in all cases of ichthyosis vulgaris and in more cases of psoriasis than in cases of acne vulgaris.

Steigleder & Elschner demonstrated (7) that the psoriasiform lamellae in cases of psoriasis, neurodermatitis constitutionalis and dermatitis dysseborrhoeica showed a more intensive activity of non-specific esterases than the stratum corneum of persons without dermatoses. Since the skin surface lipids of psoriatics were obtained from the macroscopically unchanged praesternal region, and since the maximum of free fatty acids of these lipids was often found to be more intensive than the maximum of esters, contrary to patients with acne vulgaris, it seemed that the activity of esterases in the unchanged skin of psoriatics is more intensive than the activity of these enzymes on the skin of acne patients. We must, however, admit that this difference is not significant ($P \sim 0.2$).

Nevertheless the infra red spectroscopy of the skin surface lipids is a valuable method for determination of the relationship of esters and free fatty acids in minute quantities of these substances.

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