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Determination of prostaglandin analogs in cosmetic products by high performance liquid chromatography with tandem mass spectrometry

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ABSTRACT

A method was developed and validated for the determination of 16 prostaglandin analogs in cosmetic products. The QuEChERS (Quick, Easy, Cheap, Efficient, Rugged, Safe) liquid–liquid extraction method, typically used for pesticide residue analysis, was utilized as the sample preparation technique. The prostaglandin analogs were chromatographically separated and quantified using high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). Thirty-one cosmetic products were surveyed, and 13 products were determined to contain a prostaglandin analog with amounts ranging from 27.4 to 297 μg/g. The calculated concentrations for the cosmetic products were in a similar range when compared to the concentrations of three different prostaglandin analog-containing prescription products.

1. Introduction

Eyelash and eyebrow enhancing cosmetic products have been increasing in demand and popularity in recent years. Some of the chemicals responsible for enhancements such as lengthening and darkening eyelashes and eyebrows are a class of compounds called prostaglandins [1]. Prostaglandins are used in many biological processes and have a wide variety of effects. A few prostaglandin analogs (bimatoprost, latanoprost, and travoprost) are used to control intraocular pressure, or treat glaucoma, through the administration of prescription eye drops [2–9]. Side effects of this treatment include conjunctival hyperemia, excessive tearing, inflammation, increased coloring of the iris, periocular skin pigmentation, as well as an increase in eyelash thickness and length [10–12]. These side effects that increase and enhance eyelashes gave reason to implement prostaglandin analogs for use in cosmetic products.

The prostaglandin analogs studied, including the three used as drugs for glaucoma treatment, are structurally similar (Fig. 1). They all are comprised of a cyclopentanediol backbone with two arms: one arm containing an aromatic moiety, and the other containing a carbonyl functional group. Fortunately, they are dissimilar enough to be chromatographically separated and quantified using high performance liquid chromatography with tandem mass spectrometry (HPLC-MS/MS). A few of the noted prostaglandins, along with many others, have previously been analyzed in various matrices. Many techniques, including high performance liquid chromatography paired with ultra-violet absorption (HPLC-UV) [13–16] or fluorescence detection [17,18], gas chromatography–mass spectrometry (GC/MS) [19], high performance liquid chromatography-electrospray ionization–tandem mass spectrometry (HPLC-ESI-MS/MS) [20–29], and high performance liquid chromatography–atmospheric pressure chemical ionization–tandem mass spectrometry (HPLC-ACPI–MS/MS) [30,31], have been used to determine prostaglandins contained in a wide variety of matrices ranging from in vitro enzyme incubations to pharmaceuticals and natural products.

In general, cosmetic product matrices are complex and can be completely different in composition for two products used for the same purpose. Some of these matrices include serums, oils, lotions, creams, mascaras, powders, lipsticks, etc. Sample preparation, therefore, can be challenging. Traditionally, cosmetic samples are prepared using conventional liquid–liquid extraction (LLE) and solid–liquid extraction (SLE) techniques [32]. While these conventional sample preparation techniques are useful when dealing with a variety of matrices, there are disadvantages such as use of solvent (large quantities and potentially carcinogenic) and time consuming multi-step processes. For this project, the QuEChERS (Quick, Easy, Cheap, Efficient, Rugged, and Safe) extraction method was implemented for sample preparation. The QuEChERS method was originally developed and utilized for pesticide analysis since these samples come from a large variety of matrices [33–36].

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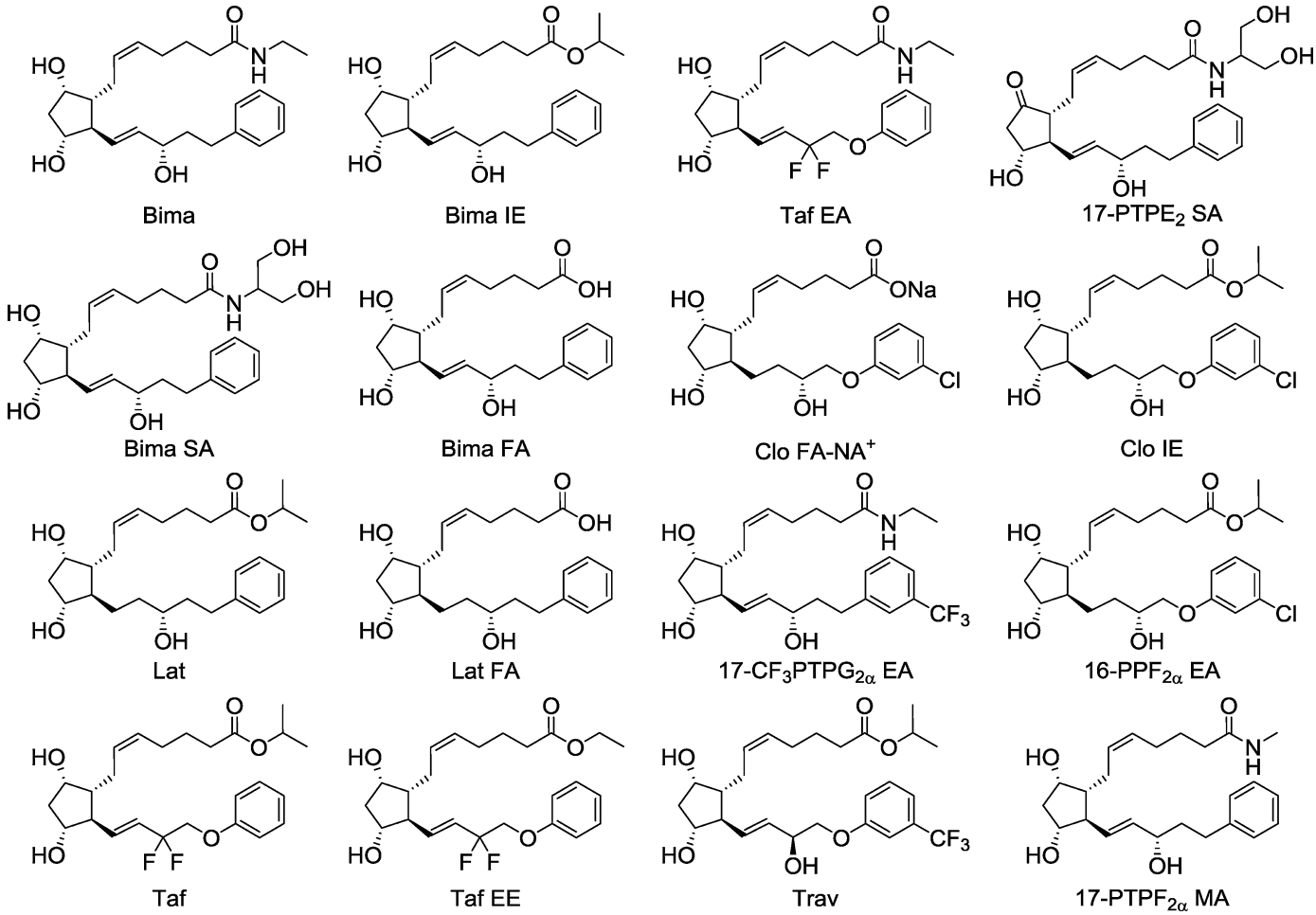

Fig. 1. Structures of the prostaglandin analogs studied.

QuEChERS was chosen for this study because it was envisioned to be a quick, easy, and cheap way to extract the relatively non-polar prostaglandin analogs from the aqueous serums and mascaras.

To date, no method has been reported for the detection and quantitation of prostaglandin analogs in cosmetics. In this study an LC/MS/MS method was developed to determine 16 prostaglandin analogs contained in a survey of 31 eyelash and eyebrow enhancing cosmetic products using four stable isotopically labeled internal standards. The QuEChERS extraction method was adopted and utilized for sample preparation of the cosmetic samples without any need for further sample cleanup. To our knowledge, this would be the first account of the QuEChERS method being used for cosmetic sample preparation. This method may be used for the detection and quantitation of the noted prostaglandin analogs in a variety of matrices.

2. Material and methods

2.1. Chemicals

LC-MS grade water (H_2O), methanol (MeOH), and acetonitrile (MeCN) were purchased from Fisher Scientific (Pittsburgh, PA). All prostaglandin analogs (bimatoprost (bima), bimatoprost isopropyl ester (bima IE), bimatoprost serinol amide (bima SA), bimatoprost free acid (bima FA), latanoprost (lat), latanoprost free acid (lat FA), tafluprost (taf), tafluprost ethyl amide, (taf EA) tafluprost ethyl ester (taf EE), travoprost (trav), (+)-cloprostenol (clo), (+)-cloprostenol isopropyl ester (clo IE), 17-phenyl trinor prostaglandin E_2 serinol amide (17-PTPE$_2$ SA), 17-phenyl trinor prostaglandin $F_{2\alpha}$ methyl amide (17-PTPF$_{2\alpha}$ MA), 17-trifluoromethylphenyl trinor prostaglandin $F_{2\alpha}$ ethyl amide (17-CF$_3$PTPF$_{2\alpha}$ MA), 16-phenoxy prostaglandin $F_{2\alpha}$ ethyl amide (16-PPF$_{2\alpha}$ EA)) and internal standards (bimatoprost-d_4 (bima-d_4), bimatoprost free acid-d_4 (bima FA-d_4), latanoprost-d_4 (lat-d_4), and latanoprost free acid-d_4 (lat FA-d_4)) were purchased from Cayman Chemical (Ann Arbor, MI). All chemicals were sold as ≥95% pure and were used without further purification. Thirty personal care products were purchased via the internet.

2.2. Instrumentation

The liquid chromatography was carried out using an Acquity UPLC® (Waters, Milford, MA) consisting of a binary solvent manager and a sample manager. The sample manager was set to 4 °C during operation. The separations were carried out using a 2.6 μm Kinetex XB-C18 column (100 mm × 2.1 mm i.d., Phenomenex, Torrance, CA) coupled to a 0.5 μm KrudKatcher ultra HPLC in-line filter (0.004 in i.d., Phenomenex, Torrance, CA). Elution was completed using a 20-min gradient program operating with a 0.50 mL/min flow rate with a 10 μL injection volume. Mobile phase A was composed of 0.1% formic acid in 95:5 H_2O:MeOH (v/v) and mobile phase B was composed of 0.1% formic acid in 5:95 H_2O:MeOH (v/v). The gradient parameters were: 0–1 min 20% B, 1–15 min 20% B to 100% B, 15–18 min 100% B, 18–19 min 100% to 20% B, 19–20 min 20% B. The LC elute was introduced to the ion source only between 7 and 12.5 min during the run using a Valco valve switch to prevent contamination.