



From Green Tea to Dibenzoylmethane Derivatives

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Charles Fox is an independent consultant to the cosmetic and toiletry industry. He was previously Director of Product Development for the Personal Products Division of Warner-Lambert Company. Mr. Fox is a past recipient of the Cosmetic Industry Buyers and Suppliers Award and the Society of Cosmetic Chemists Medal Award; he has served as President of the SCC.

Skin and Skin Care

Katiyar et al. have published a review on green tea polyphenolic antioxidants and skin photoprotection.¹ Green tea is consumed as a popular beverage worldwide, particularly in Asian countries such as China, Korea, Japan and India, and it contains polyphenolic compounds known as epicatechins, which are antioxidant in nature. Many laboratories have shown that topical treatment or oral consumption of green tea polyphenols inhibits chemical carcinogens or UV radiation-induced skin tumorigenesis in different animal models. Studies have shown that green tea extract also possesses anti-inflammatory activity. These anti-inflammatory and anti-carcinogenic properties of green tea are due to the polyphenolic constituents present therein. The major and most chemopreventive constituent in green tea responsible for these biochemical or pharmacological effects is (-)-epigallocatechin-3-gallate (EGCG).

Understanding the molecular mechanisms of green tea effects is a subject of investigation in many laboratories. Using green tea polyphenols in skin treatments has been shown to modulate the biochemical pathways involved in inflammatory responses, cell proliferation and responses of chemical tumor promoters as well as UV light-induced inflammatory markers of skin inflammation. Topical treatment with EGCG on mouse skin also results in prevention of UV B-induced immunosuppression and oxidative stress. The protective effects of green tea, either through topical treatment or oral consumption, against UV light-induced inflammatory or carcinogenic responses in human skin are not well understood. Based on beneficial effects of green tea on skin,

which has been documented extensively using mouse models and a few human skin studies, many pharmaceutical and cosmetic companies are supplementing their skin care products with green tea extracts. Therefore, the focus of this communication is to review and analyze the photoprotective effects of green tea polyphenols on skin.

Kimberly-Clark describes wet wipes containing cationic fatty acid surfactants.² The wet wipe comprises a fibrous sheet impregnated with an aqueous solution containing a cationic fatty acid surfactant having a cationic nitrogen and a fatty acid moiety with a carbon chain length 8-40. The wet wipes have improved tactile properties and cleaning efficacy without excessive skin irritation or foaming when compared to conventional wet wipes. The composition of the aqueous solution used to impregnate the wipes is shown in Formula 1.

Noevir describes skin-lightening cosmetics containing tyrosinase inhibitors.³ This invention relates to skin cosmetics which show enhanced inhibitory activities against melanin formation and prevent sun-induced pigmentation, spots, freckles, etc. The cosmetics consist of hinokitiol glycosides and substances selected from a group consisting of L-ascorbic acid (and salts or derivatives thereof), 2-hydroxycarboxylates, hydroquinone (and derivatives thereof), cysteine (and derivatives thereof), glucosamine (and derivatives thereof), azelaic acid (and derivatives thereof), placental extracts tyrosinase-inhibiting plant extracts, and algae extracts. A composition from the patent is shown in Formula 2.

Playtex Products, Inc. discusses in a recent patent sunless tanning compositions based on dihydroxyacetone, melanin, mahakanni or erythrulose.⁴ The present invention provides a sunless tanning composition having a sunless tanning agent, (selected from a group consisting of dihydroxyac-

Formula 1. Wet Wipes²

<i>Helianthus annuus</i> (sunflower) seed	
amidopropyl morpholine-lactate	2.600000
Polysorbate 20	0.200000
Tocopheryl acetate	0.010000
Sodium hydroxymethyl glycinate	0.200000
Glycerin	0.050000
Aloe barbadensis gel (200:1)	0.002500
Iodopropynyl butyl carbamate	0.001667
Fragrance (<i>parfum</i>)	0.030000
Water (<i>aqua</i>)	96.9058

Formula 2. Skin Lightening Gel³

Hinokitiol-D-glucoside	0.30%
<i>Aquilaria agallocha</i> extract	0.20
Carboxyvinyl polymer	0.50
Dipropylene glycol	8.00
Potassium hydroxide	0.10
Water (<i>aqua</i>)	qs 100.00

Formula 3. Oral Deodorant Composition¹⁰

Magnolol	1.000%
Sodium fluoride	0.243
Sorbitol solution	36.757
Precipitated silica abrasive	20.000
Triclosan	0.280
Carbomer-956	0.250
Sodium saccharin	0.150
Xanthan gum	1.100
Glycerin	2.000
Sodium alkyl sulfate solution	7.500
Polyethylene glycol-300	4.000
Flavor	0.800
Titanium dioxide	0.500
Trisodium phosphate dodecahydrate	0.900
Monosodium phosphate	0.400
Water (<i>aqua</i>)	qs 100.000

etone, melanin, mahakani, erythrose and any mixtures thereof), and an application indicator agent, (selected from a group consisting of henna, caramel and mixtures thereof). Optionally, a color fixative may be included such as an urethane polymer or a polyacrylate-polysiloxane graft polymer. The composition further comprises fragrances, citric acid, ascorbic acid and xanthan gum. The most preferred composition contains (by wt.) 0.25-8% dihydroxyacetone, 0.05-1% henna, 0.15-10% caramel, and 0.5-5% a color fixative.

Unilever discloses cosmetic skin care compositions containing pulegone.⁵ An oil-in-water emulsion skin care composition consisting of pulegone (0.001-10%); a moisturizing agent (i.e., propylene glycol, sorbitol, butylene glycol, glycerin, cetostearyl alcohol, cetyl palmitate, myristyl alcohol); and a cosmetically acceptable vehicle. The composition improves transglutaminase-1 expression and

ceramide expression, and enhances the cell uptake of glucose. It is useful in treating aged, photoaged, dry, lined or wrinkled skin.

L'Oreal describes the use of manganese in the treatment of skin wrinkles and skin paleness.^{6,7} Cosmetic compositions containing manganese or their salts are used for the treatment of skin wrinkles and paleness. The efficacy of 10⁻³ M manganese gluconate on the inhibition of phrenic nerve electrical stimulation is shown. A lotion contained 1.50% 10⁻³M manganese gluconate, 0.05% antioxidants 0.30% preservatives, 8.00% ethanol and water q.s. 100%.

Perricone discusses the treatment of skin damage using acetylcarnitine and phosphatidylcholine and/or ascorbyl fatty acid esters.⁸ Acetylcarnitine and phosphatidylcholine and/or ascorbyl fatty acid esters are topically applied to treat skin damage. Typical compositions contain about 0.025-5%, more narrowly 0.5-2% acetylcarnitine. Where employed, ascorbyl fatty acid ester concentrations range about 0.5-7%, more narrowly about 1-5%, and the esters are preferably fat-soluble and saturated. A preferred embodiment contains L-acetylcarnitine, ascorbyl palmitate and food-grade lecithin. The composition also contains an R-hydroxy acid adjunct selected from lactic acid, glycolic acid or their mixtures. The skin damage is selected from contact dermatitis, atopic dermatitis, xerosis, eczema, rosacea, seborrhea, psoriasis, thermal and radiation burns, other types of skin inflammation and aging.

Not for Reproduction **Deodorants**

Dragoco Gerberding discloses the usage of 6,10-dimethyl-5,9-undecadien-2-ol as antimicrobial agent and antiperspirant.⁹ The invention relates to the use of 6,10-dimethyl-5,9-undecadien-2-ol as an antimicrobial agent, especially for inhibiting the growth of the microorganisms that cause body odor, such as *Staphylococcus epidermidis*, *Corynebacterium xerosis* and *Brevibacterium epidermidis*. Isomers or mixtures of 6,10-dimethyl-5,9-undecadien-2-ol isomers are included in cosmetic preparations as deodorants or to treat dandruff and mycosis of the skin and nails.

The Procter & Gamble Company describes oral deodorant compositions comprising polyphenol herbal extracts.¹⁰ Disclosed are oral compositions that include an effective amount of a polyphenol herbal extract (selected from a group consisting of magnolol, honokiol, tetrahydromagnolol, tetrahydrohonokiol and mixtures thereof); an effective amount of a buffering agent; 40% to 99% aqueous carriers; and a total water content from about 5 to about 70. An example of such an oral deodorant composition is shown in Formula 3. Breath protection efficacy of the composition over 4 hours was shown in volunteers.

Hair Care

Unilever discloses leave-on or rinse-out hair conditioner compositions containing silicone quaternary compounds

Formula 4. Hair Styling and Lightening Composition¹⁴

Phosphoric acid (85%)	0.07%
PVP/vinylacetate S360	2.00
Copolymer 845 (30%)	5.00
PEG-2 oleammonium chloride (and) propylene glycol	0.30
Fragrance (<i>parfum</i>)	0.25
DL-panthenol	0.80
Polysorbate 20	0.50
Urea	0.25
Cetrimonium chloride (30%)	2.50
Hydrogen peroxide (35%)	4.35
Water (<i>aqua</i>)	qs 100.00

and thickeners.¹¹ The present invention relates to a leave-on or rinse-out hair conditioning or styling aid composition that consists of a silicone quaternary compound (0.1-6%); a cationic thickener (0.25-5%); and a carrier (i.e., water or a hydro-alcoholic solvent).

The composition is substantially lacking in fatty alcohol. The silicone quaternary compound is Quaternium 80, and the cationic thickener is a copolymer of acrylamidyl-propyltrimmonium chloride or N,N,N-trimethyl-2[(methyl-1-oxo-2-propenyl)oxy] chloride polymer. The composition further comprises 0.2-8% of a water soluble styling resin (e.g., polyvinyl pyrrolidone/vinyl acetate copolymer), 0.1-8% of a wax, and a non-quaternized silicone such as polyalkylsiloxanes, polyalkylarylsiloxanes, dimethicone copolyols, alkylamino-substituted silicones, silicone gums and crosslinked polymeric siloxanes.

In a recent patent, Shiseido describes emulsion-type hairstyling compositions.¹³ Hair styling compositions contain 1-30 % solid waxes, 0.01-5 % water soluble polymers, 1-30% oils, 0.1-10% powders and 30-90 % water.

Unilever discloses a leave-in foaming composition for styling, lightening and highlighting hair.^{14,15} A leave-in, aqueous foamable composition is described for styling, lightening and highlighting hair and consists of a styling agent, a peroxygen compound, an acid and a foaming agent. The compositions have a pH of about 5 or less. An example from the patent is shown in Formula 4.

Henkel, in a recent patent, describes a hair preparation for the treatment of dandruff using 1-hydroxy-2-pyridone derivatives.¹⁶ The invention concerns a two-component antidandruff hair preparation that consists of a shampoo and a hair tonic lotion. The shampoo contains a magnesium alkylether sulfate surfactant and a 1-hydroxy-2-pyridone derivative. The antidandruff lotion is a water-ethanol solution of the 1-hydroxy-2-pyridone derivative.

Makeup

L'Oreal describes the use of fibers in a make-up or skin-care composition for giving a matte skin appearance.¹⁷ Polymer

Formula 5. Long Lasting Lipstick¹⁸

Benzyl propoxybenzoate-terminated polydimethylsiloxane	5.00%
Polyethylene wax (Performalene 500/New Phase)	15.00
Pigments	9.00
Hydrogenated polyisobutylene oil	35.50
Phenyltrimethicone (Dow 556 Fluid)	35.50

fibers, such as particles of polyamide fibers, are used in make-up or skincare compositions that are intended to give a matte appearance to the skin.

L'Oreal, in a recent patent, also discloses a method for improving persistence of cosmetic effect or skin care effect in cosmetics and the cosmetic compositions.¹⁸ The invention relates to a method for improving persistence of cosmetic effect and/or skin care effect in a cosmetic composition containing an oily phase, wherein the method includes mixing a specified polyorganosiloxane in the composition. The composition of a lipstick using this technology is shown in Formula 5.

Veilicies

Revlon discloses cosmetic compositions containing film-forming polymers plasticized with esters of malic acid.¹⁹ A cosmetic composition for application to keratinous surfaces – such as a nail enamel, mascara or makeup – contains at least one film-forming polymer and a plasticizer which is a C1-20 ester of malic acid. A film-forming polymer is a synthetic polymer comprised of acrylic acid, acrylic acid esters and methacrylic acid esters monomers as well as a natural polymer such as hydrolyzed keratin or cellulose. An example of a sun blocking cream is shown in Formula 6.

Pfizer Products Inc. discloses an interesting skin protectant spray composition.²⁰ A liquid water repellent, substantially anhydrous spray-pumpable skin protectant composition is disclosed. The composition is designed for spraying directly onto skin, has suitable adherence to the skin and resists running. The composition contains one or more actives for whichever indication the

Formula 6. Sun Blocking Cream¹⁹

Cyclomethicone (and) trimethylsiloxy silicate (Dow Corning 749 Cosmetic Fluid)*	30.0
Iron oxide	3.5
Titanium dioxide	20.0
Zinc oxide	5.0
Boron nitride	7.8
Diethyl malate (plasticizer)	0.2
Dow Corning Silastic Q7-4350*	7.0
Hexamethyldisiloxane	10.0
Cyclomethicone	11.5
Trifluoropropylmethylpolysiloxane	5.0

* These are the film-forming polymers

Formula 7. Shaving Cream¹

Urea	0.5%
Triethanolamine	1.0
Polyoxyethylene cetyl ether (HLB 15)	3.0
Glyceryl stearate (HLB 6)	2.0
Water (<i>aqua</i>)	qs 100.00

Formula 8. Sunscreen with DNA Repair Enzymes²²

Octyl methoxycinnamate	10.00%
Octyl triazone	5.00
Caprylic/capric triglyceride	5.00
Cetyl alcohol	1.50
Plankton extract (and) lecithin	1.00
Polyglyceryl-3 methylglucose distearate	1.00
Tocopherol acetate	1.00
Butyl methoxydibenzoylmethane	1.00
Hydrogenated coco-glycerides	0.50
Cetyl palmitate	0.50
Xanthan gum	0.10
Disodium EDTA	0.10
Sodium carbomer	0.20
Ethanol	7.00
Water (<i>aqua</i>)	qs 100.00

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composition has been formulated, one or more rheological modifiers, and a carrier. The rheological modifiers help give the composition rheological properties so it can be sprayed using a spray pump dispenser (i.e., a propellant-free, non-pressurized dispenser) yet still resist running after it has been applied to the skin.

The rheological modifiers can be waxes and/or associative thickeners such as some forms of silica. The carrier can be mineral oil or a mineral oil replacement (e.g., isohexadecane, cyclomethicone). Film-forming components also help the composition resist running. One indication for which the composition may be formulated is diaper rash, in which the composition is designed for spraying onto the skin. The active ingredient for diaper rash may be dimethicone and preferably zinc oxide.

Shaving Products

Shiseido in a recent patent describes shaving compositions containing urea and surfactants.²¹ The shaving compositions range in pH from 7.5-10 at 25° and contain 0.5-3.0% urea and 0.1-10% nonionic surfactants within the HLB range of 8-20. The composition of a shaving cream at pH 9 is shown in Formula 7.

Sunscreens

Stada Arzneimittel discloses sunscreen and skin care compositions containing DNA-repairing enzymes.²² The invention concerns sunscreen and skin care hydrogels and emulsions that contain DNA-repairing enzymes such as photolyase or endonuclease. Further, the compositions contain emulsifiers and organic or inorganic sunscreens. Enzymes can be in the form of plankton extracts and are enclosed in a liposome. An example from the patent is shown in Formula 8.

In a recent patent, Unilever discusses enzymic preparation of protein-bound soluble melanin and its use as a sunscreen.²³ A process is provided for preparing protein and/or peptide-bound melanin, which is soluble in an aqueous

solution at pH 2 to 11 and at temperatures of 0° to 50°. This is done using the steps of reacting DOPA or tyrosine with an oxidant enzyme in the presence of an acidic protein and/or peptide. Soluble melanin was prepared by reaction of dl-DOPA with tyrosinase in the presence of bovine serum albumin. The soluble protein- and/or peptide-bound melanin of this invention is useful as a sunscreen.

Spirig Pharma discloses a method for the photostabilization of dibenzoylmethane derivatives using 2,4-bis-[[4-(2-ethylhexyloxy)-2-hydroxy]phenyl]-6-(4-methoxyphenyl)-1,3,5-triazine.²⁴ By using this compound, the photostability of dibenzoylmethane derivatives is considerably improved, and, a stabilization of cinnamic acid esters is also indirectly effected, with which photostable cosmetic compositions for protecting against UV radiation are made possible. These cosmetic com-

positions have a high sun protection factor and a high extinction both in the UVA as well as in the UVB range.

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References

Address correspondence to Charles Fox, c/o Editor, *Cosmetics & Toiletries* magazine, 362 South Schmale Road, Carol Stream, IL 60188-2787 USA.

1. SK Katiyar et. al, *Int J Oncol* 18 6 1307-1313 (2001)
2. WO 01 83,665 Kimberly-Clark Worldwide Inc, USA
3. JP 2001 316,241 Noevir Co Ltd., Japan
4. WO 01 85,122 Playtex Products Inc., USA
5. WO 01 85,126 Unilever PLC; Unilever N.V.; Hindustan Lever Limited, UK
6. EP 1,155,685 L'Oreal, France
7. EP 1,155,686 L'Oreal, France
8. WO 01 82,878 Perricone, V Nicholas, USA
9. WO 01 85,120 Dragoco Gerberding & Co A.-G Germany
10. WO 01 82,922 The Procter & Gamble Company, USA
11. WO 01 82,879 Unilever PLC; Unilever NV; Hindustan Lever Limited, UK
12. JP 2001 316,226 YK Nonogawa Shoji, Japan
13. JP 2001 316,228 Shiseido Co Ltd, Japan
14. WO 01 85,105 Unilever PLC; Unilever N.V.; Hindustan Lever Limited, UK
15. WO 01 85,113 Unilever PLC; Unilever N.V.; Hindustan Lever Limited, UK
16. WO 01 85,107 Henkel KAAG, Germany
17. EP 1,151,742 L'Oreal, France
18. JP 2001 316,244 L'Oreal SA, France
19. WO 01 82,866 Revlon Consumer Products Corporation, USA
20. WO 01 85,128 Pfizer Products Inc, USA
21. JP 2001 316,233 Shiseido Co Ltd, Japan
22. EP 1,153,600 Stada Arzneimittel AG, Germany
23. US 6,315,988 Unilever Home and Personal Care Division of Conopco Inc., USA
24. WO 01 85,123 Spirig Pharma A.-G., Switzerland

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