Trans Isomers in Cosmetics
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BY JAMES BROWN AND ROBERT KLEIMAN

Cosmetic chemists may soon be called upon to identify the trans isomer content of their brand’s formulations and to certify that their products are “Trans Free.” The impetus behind the movement is in part due to consumer concerns that trans fatty acids are not healthful in their diets and will be undesirable to use on their body as well. This intuitive reaction is not without merit. Trans fatty acids have been implicated in the inhibition of A5 and A6 desaturation of polyunsaturated fatty acids; i.e., the metabolic pathway to prostaglandin formation. Prostaglandins are important mediators of skin metabolism. Topical introduction of trans fatty acids may disrupt normal prostaglandin formation. The fire is also being stoked in the USA due to broad new FDA labeling proposals (World Food Chemical News, November 24, 1999, Vol. 19, Number 16) that would require the amount of trans fatty acids in a product to be listed on the “Nutrition Facts” panel of food labels. This trans fatty acid isomer phenomenon is the latest “food bane” trend to be transposed to cosmetics. Marketers will undoubtedly find a receptive audience for claims of “Trans Free” cosmetic and personal care products. The good news is that trans isomers are easy to detect, there are alternative routes to obtain “Trans Free” ingredients and naturally occurring trans isomers are rare.

CIS AND TRANS GEOMETRY

The cis- and trans-labels refer to the geometric positioning of hydro- gen atoms about points of unsaturation (double bonds) found in lipid chains. The cis isomer is simplistically represented by both hydrogen atoms of the carbon atoms forming the double bond being located on the same side of the carbon chain (see Figure 1). The trans form is depicted with hydrogen atoms positioned on opposite sides of the carbon chain (see Figure 2).

MATURE MAKES CIS FATTY ACIDS

Nature creates an overwhelming majority of cis fatty acids (and fatty alcohols) as components of lipid materials (emulsions) such as vegeta- ble oils, fats, waxes, etc., trans isomers of lipid materials occur infrequently in nature. Table 1 contains a listing of some of the relatively rare sources of naturally occurring trans fatty acid isomers. Non-natural trans isomers are usually formed when lipid materials are subjected to various chemical transformations such as partial hydrogenation, oxidation, trans-isomerization, or certain enzymatic reactions.

TRANS ISOMERS IN LIPIDS

Shani[1] studied the cis and trans isomers of jojoba oil and pointed out some differences in affinity of the two forms to silver ions, the natu- rally occurring cis form having somewhat more affinity. Trans iso- mers of lipid components are ther- modynamically more stable and generally higher in melting point than the corresponding cis form. Water-insoluble differences to achieve trans isomerization of jojoba oil and points out that partial hydrogenation and trans-isomeriza- tion of jojoba oil results in the for- mation of some trans fatty acid and fatty alcohol isomers.

Trans forms of unsaturated lipid materials can also be intentionally created through the use of a nitrous or selenium oxide catalyst and have commercial application as intermediates in various chemical reactions. Trans isomers of jojoba oil have been made (jojoba butters) by using heat in the presence of acidic benzo- nite clay. Partial hydrogenation of vegetable oils and other lipid materi- als, however, by far the most likely source of trans fatty acid isomers that subsequently enter the food and cos- metic chain of distribution. Fully hydrogenated lipid materials contain neither cis nor trans fatty acid isomers. The double bonds of a fully hydrogenated lipid have been elimi- nated by completely saturating the molecule with hydrogen. This full hydrogenation reaction makes the carbon chain less active as a site for further reaction. A fully hydrogenated lipid material has a higher melting point and is more resistant to free rad- ical formation (see Figure 1). Fully hydrogenated forms are also the most oxidatively stable of all possible chemical structures of lipids. Fully hydrogenated jojoba oil (melting point 67-70°C) contains neither cis nor trans isomers (there are no remaining double bonds in the molecule) and is frequently found as a component of lipsticks, mascara, eye shadow and other “wax matrix” type formulations.

Trans fatty acids are primarily found in the form of trans fatty acids (alcohols) in unsaturated fatty acids (alcohols) in which the hydrogens of the double bonds are on opposite sides of the molecular chain.

Figure 1. cis Double Bond

Figure 2. trans Double Bond

TRANS FATTY ACID ISOMERS IN COSMETICS

The CFTA list of Japanese Cosmetic Ingredients, 4th Edition (1999) lists seven “Partially Hydrogenated” product categories. These are: (1) Squalene 2,8-Acetyl, (2) Jojoba Oil Squalene, (3) Squalane, (4) Palmitoleic Acid, (5) Palmitic Acid, (6) Cetyl Alcohol, (7) Stearic Acid. In the USA, these INCI names do not include a “Partially Hydrogenated” category as in Japan. Formulators should be aware that “partially hydrogenated” and “selectively hydrogenated/saturated” products containing trans iso- mers are sometimes referred to the trade under the INCI names of their fully hydrogenated analogs.

A search of the CFTA Dictionary for “partially hydrogenated” revealed two products: Pentahy- drocosenal and Triethylhexyl glycerol hydrogenated rosinate. The CFTA Dictionary also includes a listing for “Jojoba Butter,” a trans- isomerized form of jojoba oil con- taining about 50% trans isomers.

ALTERNATIVES TO TRANS ISOMERS IN COSMETIC PRODUCTS

The challenge of cosmetic ingredi- ent suppliers is therefore to provide manufacturers with oxidatively stable and affordable lipid based emollients that exhibit a broad range of melting points which satisfy both isomer content and oil phase emollients with these desirable characteristics can be obtained without the forma- tion of trans isomers through a pro- cess known as “interesterification.” Rozena discussed use of this inter- esterification process to modify the melting characteristics of triglycerides using various catalysts including enzymes. Another paper by Hau- man points out that the interesterifi- cation process may be a means of addressing the growing consumer concern for trans fatty acids. Trans fatty acids that inhibit prostaglandin formation are rare in nature but can be found in partially (selectively) hydrogenated, fully hydrogenated or trans-isomerized lipid materials. Consumer awareness of the acute and nutritional effects of trans isomers in food products will lead to a heightened awareness of these compounds in cosmetics. Trans isomer presence in cosmetic ingredients is easy to detect, although often obscured due to improper, incomplete or misguid- ed labeling by ingredient suppliers. Formulators should request certification from ingredient suppliers that contain the absence of trans isomers.

GLOSSARY OF TERMS

Glycolipids: lipids, which are soluble in water that can be extracted from cells by high pressure or by organic solvents such as ethane, ether, or chloroform. Examples of lipids are mono, di and triglyc- cerides, wax esters, sebum, lecithin and phosholipids.

Fatty Acids: Generally, straight chain compounds, from three to twenty-four carbon atoms in chain length, having a terminal carboxyl group. These compounds make up the bulk of fats and oils and are important in skin nutrition.

Fatty Alcohols: Generally, straight chain compounds, from three to twenty-four carbon atoms in chain length, having a terminal hydroxyl group.

Trans isomers: Fatty Acids (Alcohols): Unsaturated fatty acids (alcohols) in which the hydrogens of the double bonds are on opposite sides of the molecular chain.
cis Fatty Acids (Alcohols): Unsaturated fatty acids (alcohols) in which the hydrogens of the double bonds are on the same side of the molecule chain.

Hydrogenation: The addition of hydrogen atoms or molecules to unsaturated carbon chains (carbon chains with double bonds).

Saturation: Adding the maximum number of hydrogen atoms to an unsaturated bond. In the case of a double bond it is the addition of two hydrogen atoms, i.e., H₂.

Partial Hydrogenation: Incomplete addition of hydrogen to an unsaturated material leaving some double bonds not saturated, also known as "selective saturation" or "selective hydrogenation" or "brush hydrogenation." Partial, brush or selective hydrogenates (saturates) contain unwanted trans isomers.

Interestereification: The catalyzed chemical reaction between two or more esters in which the acids and alcohols present are recombined in a random order, also known as transesterification. This reaction does not alter the double bond geometry of unsaturated compounds, i.e., no trans isomers are formed as a result of interesterification reactions.

Transomterization: The catalyzed chemical reaction converting natural cis double bonds to trans isomers. Transomterization creates unwanted trans isomers.

REFERENCES

### Table 1. Sources of Naturally Occurring Trans Fatty Acid Isomers

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<td>Asters et al., Lipid 1966</td>
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<td>Grimaldi et al., Lipid 1966</td>
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<td>trans-9,12-Octadecenoic</td>
<td>HO</td>
<td>Tronice stans, Hopkins et al., J. Chem. Soc. 1965</td>
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<tr>
<td>cis-9,11-Octadecenoic</td>
<td>HO</td>
<td>Atheros fordii (bog oil), Cramb et al., J. Chem. Soc. 1957</td>
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<tr>
<td>4-10,12-Octadecenoic</td>
<td>HO</td>
<td>Licorice glandis (switch oil), Brown, Buettner, J. 1935</td>
</tr>
</tbody>
</table>

BY JAMES BROWN AND ROBERT KLEINMAN

In Part 1 of this series the authors point out the growing consumer awareness of trans fatty acids due to their antiinflammatory effect in food products. New FDA labeling laws proposaly for foods containing these lipid forms will draw further attention to trans isomers. Earlier research18 has revealed that some monounsaturated fatty acids inhibit the D5 and D6 desaturation of polyunsaturated fatty acids; i.e., the metabolic pathway to important prostaglandin formation. Cosmetic industry marketers will undoubtedly find a receptive audience for "Trans Free" product claims in the future.

MOTHER NATURE CREATES "CIS" ISOMERS

The majority of all lipids produced by nature contain only "cis" isomers. Trans isomers are produced when natural lipids (emollients) are manipulated through partial hydrogenation, selective saturation or transesterification reaction conducted to alter the physical characteristics of the lipid.

INTERESTERIFICATION PRODUCES NO TRANS ISOMERS

The interesterification reaction used to produce trans free emollients is one in which a fully hydrogenated lipid material (no trans isomers) is reacted with neat oil containing only cis isomers. The resulting product is an isomerous mixture of partially saturated, saturated and unsaturated esters that contain no trans isomers. This route to produce "Trans Free" oxidatively stable emollients with a broad range of melting characteristics is considerably less practiced and more expensive than the partial (or selective) hydrogenation, selective saturation or transesterification reaction, all of which produce unwanted trans isomers.

JOJOBA ESTERS: AN INTERESTERIFICATION MODEL FOR "TRANS FREE" LIPID EMOLLIENTS

Jojoba Esters are an ideal model to use to demonstrate the trans free interesterification reaction and the properties of the resulting components. The CTFA Ingredient Dictionary defines Jojoba Esters as: A complex mixture of esters produced by the transesterification/interesterification of Simmondsia Chinensis (jojoba) Oil, Hydrogenated jojoba Oil, or a transesterification mixture of the two. Figure 4 represents the interesterification reaction between (I) jojoba oil (only cis isomers) and (II) fully hydrogenated jojoba oil (no cis or trans isomers). This interesterification reaction is similar to a game of lipid "musical chairs." In this reaction the ester linkages between the jojoba acid and the jojoba alcohol in both reactants are unbalanced, liberating the saturated and unsaturated jojoba alcohols and acids so that they move about freely (and separately) in the reaction vessel. When the music stops the reaction is complete. The meandering alcohols and acids mix together (and separately) in the reaction vessel. The result is a complex blend of various old partners find each other again (randomized 1a with 1b and randomized 1a with 1b). At the same time, some new bonds are formed as saturated alcohols link with unsaturated acids (1a with 1b) and unsaturated alcohols link with saturated acids (1b with 1a). The result is a statistically randomized and isomorphous mixture of jojoba Esters, partially saturated jojoba and fully saturated jojoba.

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Esters. No trans isomers are formed during this interesterification reaction. Table 2 illustrates the range of properties achievable through this interesterification process that is used to produce "Trans Free" Jojoba Esters.

**LABELING INCONSISTENCIES**

"Jojoba Esters" have been registered for use in Japan under the existing Japanese Cosmetic Ingredient Code (JCIC) category of "Partially Hydrogenated Jojoba Oil" even though these Jojoba Esters contain no trans isomers. Conversely, some products are offered in US, Asian and European markets containing trans isomers while bearing the INCI name "Hydrogenated Jojoba Oil". These mislabeled products are in fact Partially Hydrogenated (or Selectively Saturated) Jojoba oil. Other suppliers offer simple mixtures of Hydrogenated jojoba oil and jojoba oil and unknowingly mislabel these blends as "Jojoba Esters". Jojoba Butter contains about 50% trans isomers is offered to the trade under the "Jojoba Esters" INCI designation although the product is said to be produced by "trans-isomerization" and does not conform to the INCI definition for Jojoba Esters. The message to formulators is to either conduct simple tests to determine the absence of trans isomers and/or request appropriate certification from suppliers.

**TRANS ISOMER ANALYSIS**

It is possible to determine if a lipid material contains trans isomers through a number of different analytical methods. The fact that trans isomers absorb infrared light at 900 to 1000 μm is routinely used to quantify the presence (or absence) of these isomers. Partially hydrogenated jojoba oil can be shown to have trans isomers as evidenced by the IR Spectrum absorption peak highlighted in figure 5. The same IR Spectrum was determined for jojoba Esters 60 and the lack of an absorption peak in figure 6 at the 900 to 1000 μm range is proof that trans isomers are not present.

**"FEEL" AND "SLIP" JOJOBA DERIVATIVES**

The tactility properties of partially hydrogenated jojoba oil (with trans-isomers) differ considerably from those of jojoba Esters (cis only isomers), both having the same melting point. The trans containing partially hydrogenated isomers result in a more "grainy" and "rough" texture when applied to the skin as compared to the isomorphous and more elegant "dry emollient" characteristic of randomized and trans free Jojoba Esters. To demonstrate this difference in skin feel an expert panel of thirteen individuals were asked to simultaneously apply and rub in single 0.25 gram quantities of jojoba Esters and Partially Hydrogenated Jojoba Oil on the volar forearm area. The materials tested both exhibited melting points of 59°C. Panelists were asked to complete a questionnaire that required the panelists to select rating for the "skin feel" of the sample during a) application; b) rub in; and c) five minutes after rub in. The rating scale was 1-5, with the higher ratings indicating a "smoother" skin feel. The results of the testing indicated that the overwhelming majority of all panelists considered Jojoba Esters to be "smoother" when applied and rubbed into the skin as compared to Partially Hydrogenated Jojoba Oil (containing trans-isomers). The panelists felt that the Partially Hydrogenated Jojoba Oil had a much "grasser" feel than the corresponding "trans free" Jojoba Esters. A further indication of the tactile differences in a lipid material containing either cis or trans isomers was quantified by measuring the "slip" of Jojoba Esters vs. Partially Hydrogenated jojoba Oil according to the method of Cadicamo. The procedure was modified by substitution of filter paper for the "membrane" used by Cadicamo and by use of a modified lipstick breakage meter (Challain LDM-10) to gradually increase the inclination of the plane upon which the "slip" was being determined. In the test Jojoba Esters 30 and 60 (no trans) and two Partially Hydrogenated jojoba Oil (with trans) samples with identical melting points were examined.

To perform a slip test on a material in question using the Cadicamo method, a mixture of 99% lubricity base (10% myristyl lactate, 30% iso-propyl myristate and 60% oleyl alcohol) and 1% test material is used. A 41 mm disc made from Fisher P2 filter paper is soaked in the test solution for at least 5 minutes. After the soak, the disc is removed from the solution and the excess solution is allowed to drip off until only a thin layer of test material remains on the disc. The glass incline plane is set to a very low angle and the soaked disc is placed on the top of the incline plane. The 200g weight is placed on top of the soaked disc and allowed to sit in this position for at least one minute. The instrument is set so that the end of the incline plane will increase in height at a constant rate in each trial. The movement of the incline plane is stopped at the exact moment that the weight and disc begin to slide on the inclined glass plane and the angle of the plane is reported. The Floratech slip test method is very similar to the Cadicamo method. The only difference is that in the method, the lubricity base is not used. Every material is tested at 100% concentration in the case of room temperature solid materials, the solid is melted and the filter paper disc is soaked in the melted material. Remove the paper and let the excess material drip off. The disc is then tested.

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**Tables and Figures**

Table 2: Chemical and Physical Properties of Jojoba Esters

Table 3: AOCS Methods Used to Determine Trans Unsaturation

Table 4: Physical Properties of Interestereified Jojoba Esters in Comparison with Unsaturated Partial Hydrogenates

Figure 4: IR of partially hydrogenated jojoba oil with trans absorption peak

Figure 5: Jojoba Esters 11(25) and 12(19)
remaining material will solidify on the disc in a uniform thin layer. The disc may then be tested under the same procedure shown above. However, a new disc must be used each time since the material ‘permanently’ coats the discs.

The Cadicamo slip test method was used to compare Jojoba Esters 60 to its partially hydrogenated jojoba oil analog, and Jojoba Esters 30 to its partially hydrogenated jojoba oil analog (Table 4). In each case the Jojoba Ester had better lubricating properties (smaller slip angle). Therefore, it can be concluded that, in general, Jojoba Ester samples have better slip properties than partially hydrogenated jojoba oil samples.

**CHEMICAL PROPERTIES**

Iodine Value (IV) and Refractive Index (RI) of lipid materials are two measures commonly used to follow the progress of commercial hydrogenation reactions. Fully Hydrogenated Jojoba Oil exhibits an IV of less than 2 and an RI of 1.4368 @ 80°C. Iodine Values for Hydrogenated Jojoba Oil in this range indicate that the double bond positions of the molecule comprising jojoba oil have been completely filled or “saturated” with hydrogen. The melting point of this Fully Hydrogenated Jojoba Oil is 68-70°C and it contains neither cis nor trans isomers.

In addition to the differences in skin feel and slip, the trans free Jojoba Ester will exhibit a lower IV than its trans analog when both are at the same melting point. This phenomenon is due to the trans isomer being thermodynamically more stable and therefore requiring a higher temperature to melt than the cis form of a Jojoba Ester with an identical IV. This phenomenon and other chemical and physical properties are further demonstrated in Table 4 where Jojoba Esters are compared to partially hydrogenated jojoba derivatives exhibiting identical melting points.

*Trans* isomers of fatty acids that inhibit prostaglandin formation are rare in nature but can be found in partially hydrogenated, selectively saturated or transisomerized lipid materials. Consumer awareness of the anti-nutritional effects of *trans* isomers in food products will lead to a heightened awareness of these compounds in cosmetics. *Trans* isomer presence in cosmetic ingredients is easy to detect, although often obscured due to improper, incomplete or misguided labeling by ingredient suppliers. Formulators should request certification from ingredient suppliers that confirm the absence of *trans* isomers.

**REFERENCES**