An Aroma Chemical Profile

Ethyl Methyl Phenyl Glycidate

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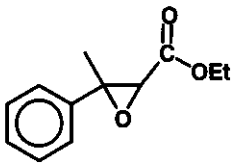
Ethyl methyl phenyl glycidate! With its several deceptive alternate names, this compound embodies the art of confusion. It belongs to a group of flavor and fragrance materials that illustrate the type of nomenclature prevalent in the aroma chemical industry in the first few decades of this century.

When they were developed (1905-1910), the glycidic esters—such as ethyl methyl phenyl glycidate—were new magic bullets used in the flavor and fragrance industry to create unique formulas. Their existence was therefore a closely guarded secret. The names given to these chemicals were used to hide their true chemical identity not only from competitors, but often as not from the flavorist or perfumer who created formulas with them. Thus began the industrial tradition of using trivial and non-chemical nomenclature to identify aroma chemicals. The custom continues today and has spread to include not only aroma chemicals, but also bases and specialties (or whatever else firms call their trade secret materials).

This group of glycidic esters aptly illustrates this phenomenon, since the esters are seldom referred to by their chemical name. A quick viewing of the alternate names used to identify these materials reveals the razzle-dazzle used to obscure their true nature.

These names often denoted an organoleptic property that was meaningless or deliberately confusing. For ex-

Ethyl Methyl Phenyl Glycidate



Mwt 206 $C_{12}H_{14}O_3$
FEMA 2444
CAS 77-83-8

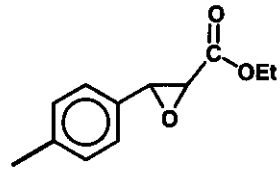
Classification: Aromatic epoxy ester

Physical Data:[1-3]

Appearance:	colorless to slightly yellow viscous liquid
Specific Gravity 25/25°C:	1.088-1.094
Refractive Index 20°C:	1.503-1.507
Boiling Point:	150°-153°C at 8 Torr
Flash Point:	>100°C
Solubility:	insoluble in H_2O; soluble in 70% ethanol, most alcohols, esters, ketones, chlorinated and aromatic hydrocarbons and natural

Additional Names:[4,5]
ethyl-3-methyl-3-phenyl glycidate
ethyl-a,b-epoxy-b-methyl phenyl propionate
E.M.P.G.
strawberry aldehyde
aldehyde C-16 (so called)
fraise
fraiseol

Ethyl para-Methyl Phenyl Glycidate



Mwt 206 $C_{12}H_{14}O_3$
FEMA Not listed
CAS 52788-71-3

Classification: Aromatic epoxy ester

Physical Data:[1-3]

Appearance:	colorless to slightly yellow viscous liquid
Specific Gravity 25/25°C:	1.010-1.050
Refractive Index 20°C:	1.480-1.520
Boiling Point:	145°-147°C at 4 Torr
Flash Point:	>100°C
Solubility:	insoluble in H_2O; soluble in 70% ethanol, most alcohols, esters, ketones, chlorinated and aromatic hydrocarbons and natural oils

Additional Names.[4,5]
ethyl-3-(p-methylphenyl) glycidate
ethyl-a,b-epoxy-b(para-methylphenyl) propionate
ethyl p-tolyl glycidate
raspberry aldehyde
aldehyde C-20 (so called)
aldehyde C-17 (sometimes called)
ethyl para-M.P.G.

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ample, fraiseol is not an alcohol and aldehyde C-16 is not an aldehyde. The term *aldehyde* was applied to these new products to convey their power or high impact.

Sometimes a name reflected uncertainty on the part of the chemist as to the exact structure of the molecule created. The Polak & Schwarz Ltd catalog of 1927 states that "Aldehydes C-14 to C-20 (fancy) are no true aldehydes as to their structure, but belong to quite other series of organic compounds; for instance aldehyde C-14 is a lactone and C-16 is an ester, while the structure of aldehyde C-18 and C-20 is not definitely known. However, in most of the price lists these bodies are to be found as aldehydes, and it would be difficult to give other names to them, as they give the same effects as aliphatic aldehydes and are to be employed in the same way."[6]

A further complication was the nature of the Darzens-Erlenmeyer-Claisen condensation that generated these products. The reaction gave low yields and produced various by-products that so colored the organoleptic profile of the resulting glycidic ester that many manufacturers of these esters did not recognize the product they had synthesized when they encountered the same ester made by another firm. Thus, the purity problems involved with this synthesis helped extend the impression that these materials were many products and of an unknown nature.

Since 1927, purification methods have improved and the marketplace has evolved. Today there is just a handful of producers, and the glycidic esters available in the marketplace have a fairly reproducible organoleptic quality.

Natural Sources

Neither of these two glycidic esters has been found in nature.

History

The glycidic esters were unknown to organic chemists until 1900, when Erlenmeyer[7] reported their preparation via the condensation of chloroacetic acid esters with ketones.

Erlenmeyer's work remained only of academic interest until it was reinvestigated by Darzens in 1904.[8] Darzens was an academic chemist, but he also had close ties to the French fragrance and flavor industry. He discovered amyl salicylate and saw it rapidly adapted by the perfumers Rouche and Armingeat, and then by Ernest Beaux for his milestone creation *Trefle Incarnat*. The exact date when amyl salicylate was first synthesized and then used as an aroma chemical is historically vague, perhaps again due to the growing policy of trying to keep "new specialties" a secret. From the time Darzens published his papers on the glycidic ester condensation, almost immediately every firm interested in aroma chemicals began exploring the reaction of chloroacetic acid esters with every commercially available aldehyde and ketone. The chemical literature is full of references to their results, but the marketplace today shows that only a few of these products survived the test of time.

The Darzens-Erlenmeyer-Claisen condensation can be viewed as a two-step reaction. The first step yields the glycidic esters; the second step furnishes our industry with substituted aldehydes, such as aldehyde C-12 MNA. The reaction proceeds as shown in Figure 1.

Thus, through this reaction, the glycidic ester can act as an intermediate that produces other valuable aroma chemicals. For example, using the raw material methyl nonyl ketone in this reaction produces the aroma chemical methyl nonyl acetaldehyde (aldehyde C-12 MNA) in Step 2. With acetophenone as a raw material, this reaction produces the

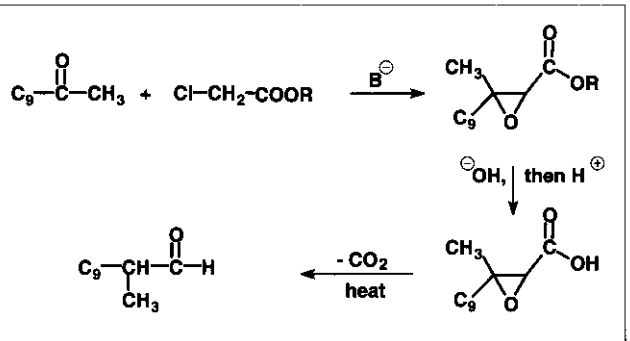

Figure 1. Glycidic esters and aroma chemicals from the Darzens-Erlenmeyer-Claisen condensation

aroma chemical ethyl methyl glycidate in Step 1 or (if more heat is applied) α-phenyl propionaldehyde in Step 2.

Prior to World War I, the glycidic esters were a relatively unknown product on the commercial market, but they were used as an in-house specialty for both flavors and fragrances. By the 1920s, the use of fruity notes in perfumes (*Mitsouko* 1921, Guerlain) and the fact that no really effective group of aroma chemicals was available to formulate an artificial strawberry or raspberry led to increased use of the glycidic esters. Aldehyde C-16 became a popular additive for lipstick fragrances, where its fruity-jam notes blend well to cover the base odor of ingredients such as castor oil and stearic acid. Until the 1960s, both aldehyde C-16 and C-20 were used in various parts of the world to create the flavor of those wonderful hard candies whose flavor we now call "red."

The work of Stollar at Firmenich uncovered the true nature of raspberry flavor in 1961, and rapidly led to vastly improved flavors and a reduction in the use of glycidic esters in the flavor area. One should note Broderick's remark that aldehyde C-16 is not a necessary ingredient to a strawberry flavor.[9] However, the use of glycidic esters in cosmetics, candle fragrances and potpourri novelties continues as a major application area today.

The chemical nature of the glycidic esters (i.e., the epoxy ring) imparts instability to these products. One might look upon them as an alkyl-aryl substituted ethylene oxide. They are chemically reactive and open up in aqueous media, losing their odor contribution. Their reactivity increases as the system pH moves away from a neutral pH of 7. They are insoluble in water, but have been used effectively in pH-neutral alcoholic media, where ethanol solubilizes them. However, the glycidates perform best in hydrophobic systems (waxes and oils); hence their major application area today is lipstick and candle fragrances.

World Consumption

The world consumption of glycidic esters in the flavor and fragrance industry in 1996 will consist of only three materials: ethyl methyl phenyl glycidate (E.M.P.G.), ethyl phenyl glycidate (E.P.G.) and ethyl-3-(para-methylphenyl) glycidate (E para-M.P.G.). The total volume of world consumption of these three items for 1996 is estimated at 1,366,600 kg (Table I).

Pricing

Over the last decade, the prices of all three of these esters have been fairly stable. This is probably due to the fact that there are few active commercial suppliers, but many potential producers. Some F&F houses manufacture these items

Table I. World consumption of glycidic esters in 1996 (estimated)

Region	Flavors (kg)	Fragrances (kg)	Total (kg)
North America			
E.M.P.G.	600	500,000	500,600
E.P.G.	600	50,000	50,600
E para-M.P.G.	0	50,000	50,000
Subtotal			**601,200**
Europe			
E.M.P.G.	0	500,000	500,000
E.P.G.	0	50,000	50,000
E para-M.P.G.	0	50,000	50,000
Subtotal			**600,000**
Other			
E.M.P.G.	200	150,000	150,200
E.P.G.	200	10,000	10,200
E para-M.P.G.	0	5,000	5,000
Subtotal			**165,400**
World Total			
E.M.P.G.	800	1,150,000	1,150,800
E.P.G.	800	110,000	110,800
E para-M.P.G.	0	105,000	105,000
Grand Total			**1,366,600**

for in-house consumption if the market price gets too high, thus putting a check on the market. However, in late 1995 significant amounts of E.M.P.G. from Romania began to appear in the U.S. market, and prices fell from their previous levels of $8–12/lb to the $7/lb level that prevails today. Prices for real aldehyde C-20 (E para-M.P.G.)—not the compounded mixture—have remained stable, for now, in the $10–16/lb range. And, aldehyde C-16 (strawberry aldehyde or E.M.P.G.) is priced in the $9–15/lb range.

Imports

Imports of glycidic esters into the U.S. over the past two decades have been at nominal levels (Table II). The year 1995 saw the traditional market turned upside down by the importation of more than 100,000 kg of E.M.P.G. from Romania.

World Producers

At least nine commercial manufacturers of glycidic esters can be identified, including China (Table III). There may be as many as three manufacturers in China alone. In addition, a number of F&F houses produce glycidic esters for in-house use, so the actual number of manufacturers may be as high as 15-20 firms.

Substitutes

These three glycidic esters have proven non-essential for their older use of creating strawberry and raspberry flavors. They have been replaced with combinations of the six materials shown in Figure 2, along with various other

Table II. Average imports (CSI estimates) of glycidic esters into the U.S. 1974-1994

Glycidic ester	Imports (kg/yr)
E.M.P.G.	600
E.P.G.	600
E para-M.P.G.	350

Table III. Manufacturers of glycidic esters

Firm	E.M.P.G.	E.P.G.	E para-M.P.G.
Arochem (India)			x
Arofine (India)	x	x	
China	x	x	x
Dragoco	x	x	
Elan	x		
Givaudan-Roure	x	x	x
Haarmann & Reimer	x		
Shiono			x

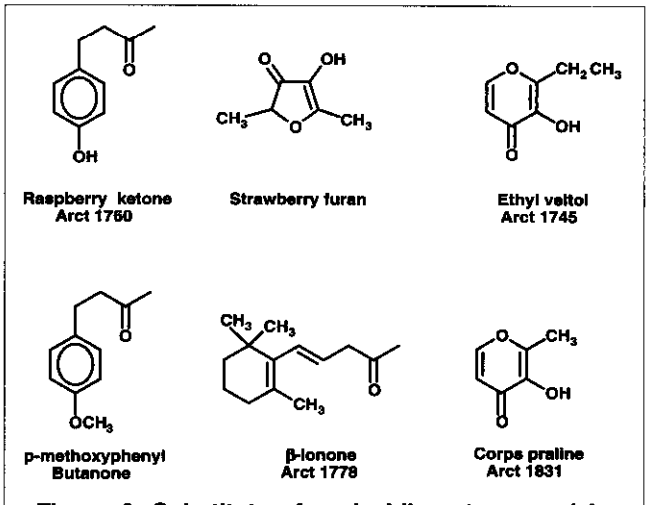

Figure 2. Substitutes for glycidic esters used in creating strawberry and raspberry flavors

additives such as leaf alcohol and its esters. In their current application areas of lipstick and candle fragrance, they are hard to replace for the value they give. These six materials now form the base for strawberry and raspberry flavors, as the three glycidic esters once did.

In addition to the additives mentioned above and the usual standard fruit building blocks such as ethyl butyrate, ethyl methyl butyrate and the cinnamate esters, various aliphatic acids have been introduced via flavor research during the last decade. The aliphatic acid 2-methyl-2-pentenoic acid* and selected sulfur compounds now allow the flavorist to come fairly close to creating a true natural berry flavor.

Analogs

Since Darzens published his work in 1904, every con-

* Strawberriff from IFF

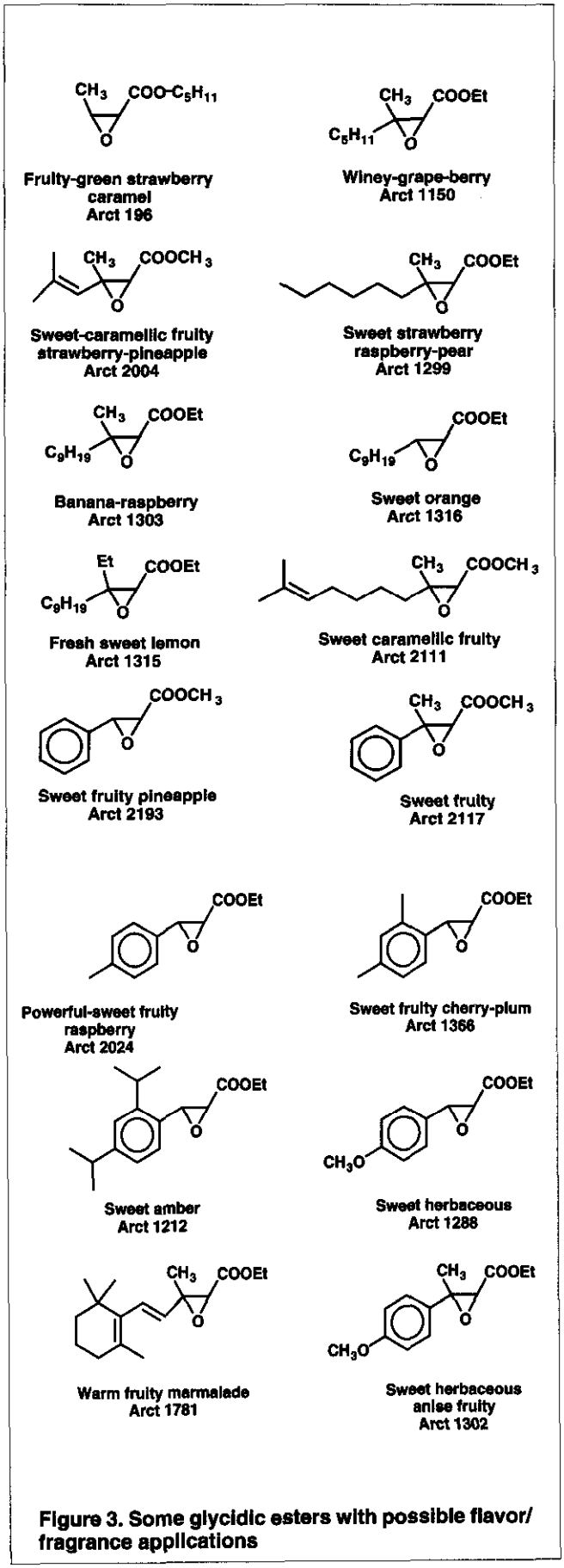

Figure 3. Some glycidic esters with possible flavor/fragrance applications

ceivable glycidic ester has been prepared and examined for its odor and flavor properties. Few of these esters have proven to be of any lasting value to the industry. A brief presentation of this effort is given in Figure 3.

Derivatives

The glycidic esters are too chemically unstable to allow the making of derivatives that still contain the oxirane ring. The group of α-substituted aldehydes such as aldehyde C-12 MNA may be considered derivatives in one sense, but some could argue that point.

References

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