

## An Aroma Chemical Profile

# Coumarin

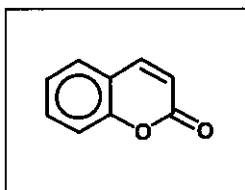
By George S. Clark, Commodity Services International, Inc., Easton, Maryland

Coumarin has an organoleptic impression that is difficult to convey in this modern era. The most graphic terms used are "hay-like" and "new-mown hay," perhaps a relic from the horse and buggy era. The same terminology is used for the poisonous gas phosgene, which does not smell like coumarin. For the "new-mown hay" description, a clarification is needed. A field of hay or grasses cut in the early morn and allowed to dry in the summer sun will exude a beautiful, sweet aromatic coumarin odor in the late afternoon and evening hours. That odor is gone by next morning. Few of us, however, are fortunate enough to experience this given today's more urban lifestyle. The description of new-mown hay is valid, but elusive in today's world. Coumarin may be described as a sweet, aromatic,

creamy vanilla bean odor with nut-like tones that are heavy, but not sharp or brilliant. Coumarin has a burning, bitter taste when concentrated, but this effect fades to a sweet herbaceous impression when coumarin is dilute. It blends well and does not stand out.

In the past, when there were numerous suppliers of coumarin and production resulted from various processes with varying degrees of sophistication, there were real problems with organoleptic profiles; by-products from the processes would color the impression. Today, the Rhone-Poulenc material has become the industrial standard against which the Chinese production is compared. Material from the former USSR is seldom seen in the West (although some of this product goes to France even today), so its

## Coumarin



Mwt 146 C<sub>9</sub>H<sub>6</sub>O<sub>2</sub>  
**FEMA/GRAS** - Forbidden;  
 not to be used in flavors  
**CAS** 91-64-5

### Classification:

benzenoid α-, β-unsaturated lactone

### Physical Data:

**Appearance:** colorless-white orthorhombic crystals or crystalline powder  
**Specific Gravity:** 20°C  
**Melting Point:** 68°-70°C  
**Boiling Point:** 297°-299°C  
**Flash Point:** >200°F  
**Vapor Pressure at 20°C:** 0.1 mmHg  
**Solubility:** 0.25 g/100 ml H<sub>2</sub>O at 20°C; very soluble in ethanol, DEP, benzyl benzoate, aliphatic and aromatic esters and ethers, chlorinated solvents, acetic acid and essential oils

### Additional names:<sup>1-3</sup>

1,2-benzopyrone  
 benzo-α-pyrone  
 5,6-benzo-2-pyrone  
 [2H]-1-benzopyran-2-one  
 2-oxo-[2H]-1-benzopyran  
 ortho-hydroxycinnamic acid lactone  
 ortho-hydroxycinnamic acid-δ-lactone  
 cis-o-coumaric acid lactone  
 3-[2-hydroxyphenyl]-2-propenoic acid-δ-lactone  
 coumarinic anhydride  
 Tonka bean camphor  
 Tonka camphor  
*French:* Coumarine  
*German:* Cumarin  
*Spanish:* Cumarina  
*Portuguese:* Cumarina

organoleptic profile is still largely unknown.

Gone are the days when coumarin was so expensive that adulteration with acetanilide or terpin hydrate had to be expected and monitored. Today, the perfumer is blessed with a quality, reproducible material.

### Natural Sources

Coumarin itself is widely distributed in the plant kingdom, but not as its glucoside.<sup>4</sup> Moreover, coumarin derivatives are widely distributed, but there are few plants found with useable concentrations of coumarin or its derivatives. Some 129 essential oils and extracts were reviewed by Lawrence<sup>5</sup> between 1988 and 1993. Only four of them contained coumarin, and then in mostly trace concentrations. They are the following:

- Tonka bean (*Dipteryx odorata* Wild.)
- Deer tongue (*Trilisia odoratissima* Walt.)
- Woodruff (*Asperula odorata* L.—old name; *Galium odoratum* L.—new name)
- Clover flowers and leaves (*Melilotus officinalis* and *alba*)

Traces of coumarin have been found in the following:

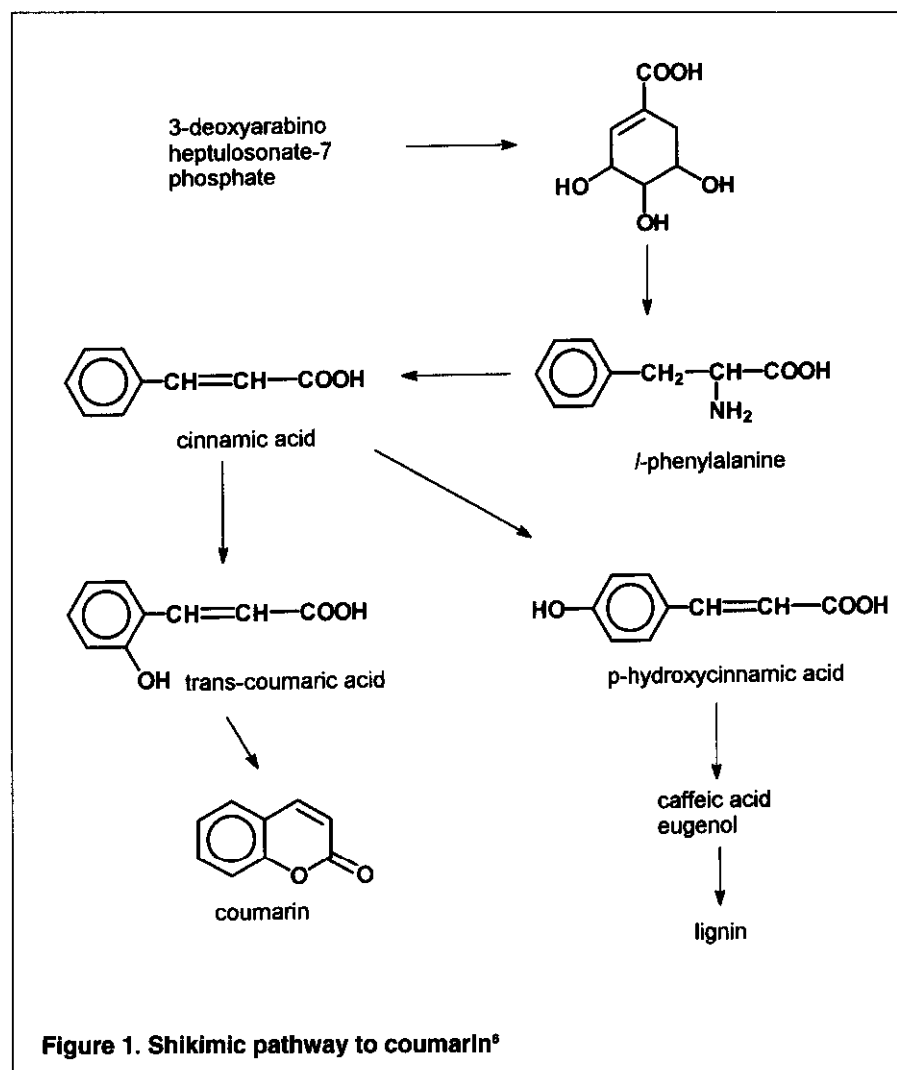
*Narcissus* species<sup>22</sup>  
*Artemisia asiatica*<sup>23</sup>  
*Matricaria recutita*<sup>24</sup>  
 tobacco<sup>25</sup>  
*Artemisia vulgaris*<sup>26</sup>  
 lavandin<sup>27</sup>  
*Thapsia gargarica*<sup>28</sup>  
*Michelia champaca*<sup>29</sup>  
 cinnamon bark<sup>30</sup>  
*Cinnamomum esmopholeum*<sup>31</sup>  
 cassia<sup>32</sup>  
 annual wormwood (*Artemisia annua*)<sup>33</sup>  
*Orchis militaris*<sup>34</sup>  
*Cinnamomum sieboldii*<sup>35</sup>  
*Melilotus caspius*<sup>36</sup>  
 wild vanilla orchid  
 spike lavender oil  
 Ganet absolute  
 Daphne  
 green tea leaves

Even the best-known source of natural coumarin, Tonka beans, contains only 1-3%, by weight, of this material. At this level, the Tonka bean is usually used as an alcoholic extract. No natural coumarin is isolated and offered commercially.

The lack of a variety of plant species with a high concentration of coumarin is surprising, as it is generated as part of the Shikimic acid pathway to lignin (Figure 1). Other intermediates (such as cinnamic aldehyde and eugenol) in this extended series are found in useable concentrations in plants.

### History

The usage of coumarin as a pure synthetic chemical has little more than a 100-year history. But its use as an ingredient in fragrances and flavors, as a result of its inclusion in essential oils, extracts, herbs and spices, goes back to the dawn of history. In Germany, a springtime custom going back to the Pagan era calls for preparing a Maibowle (May Punch) containing white wine, strawberries and woodruff (Waldmeister). The key ingredient in woodruff is coumarin, and the Maibowle's flavor clearly reflects coumarin's presence. The popularity of the custom resulted in the marketing of Maiwein (May wine), a doctored second-grade white wine, flavored with Waldmeister. Before the demise of coumarin, these wines were heavily



flavored. However, today (if you can find a bottle), the flavor is barely detectable. In the dawn of organic chemistry, Vogel<sup>7</sup> investigated Tonka beans in 1820 and reported a substance which was later named coumarin by Guibourt,<sup>8</sup> who thought the substance was either benzoic acid or a kind of camphor. Boullay and Boutron-Charlard<sup>9</sup> confirmed the uniqueness of coumarin. In 1844, Kosmann<sup>10</sup> reported its presence in woodruff. Then there was little further activity in the area of coumarin until Perkins discovered a synthetic method for its preparation in 1868.<sup>11</sup>

At this point, a minor historic conflict arises as to when the first commercial production of coumarin started. Boisdé and Meuly<sup>12</sup> maintain that all the coumarin consumed commercially prior to 1890 was of natural origin. However, it is well documented that by this time Haarmann & Reimer was supplying commercial amounts of synthetic coumarin. Their production began in 1876. Shortly after, Schimmel & Co. of Leipzig, Germany, and Hugo Weil<sup>13,14</sup> in France began supplying synthetic coumarin. In 1882, Paul Parquet of Houbigant<sup>15</sup> created the perfume and soap fragrance *Fougere Royale*, which was based upon bergamot oil and synthetic coumarin. This is looked upon as a milestone in perfumery, as it marks the beginning of the use of synthetic aroma chemicals and, thus, the modern era of the fragrance industry.

These seemingly conflicting references can best be explained by how one defines "commercial." The volumes of production for aroma chemicals in the 1800s were laboratory-scale at first by today's standards. Only in the late 1800s did they increase to what modern chemists would consider pilot plant scales. Most fragrance houses maintained close associations with university chemistry departments and key professors working in the field of synthetic aroma chemicals and natural isolates. They did this in order to obtain not only news of the latest advances in the field, but also supplies of the new synthetic aroma chemicals generated by those professors' students in their organic prep labs. Universities had to prepare most of their own organic chemicals for research purposes because commercial laboratory supply houses were almost nonexistent. Thus arose the custom of university laboratories generating low volumes of organic chemicals for sale to outside parties. In some cases, this relationship led to the formation of organic chemical supply firms which were a direct outgrowth of university activities.

If we examine a "typical" *Fougere* formula<sup>16</sup> with a 15% loading of coumarin and assume that a 2% loading of the fragrance would be typical in the soap marketed, then a quick calculation demonstrates that 150 kg of synthetic coumarin will generate 1,000 kg of fragrance concentrate, which in turn will provide 25,000 kg of perfumed soap (2% fragrance loading) and 160,000 one-ounce bottles of perfume (20% oil loading).

In 1880, fragrances were not mass marketed, and I doubt if Houbigant's customer base, including export orders, totaled more than 5,000 accounts at this time. Thus, 150 kg of coumarin produced in a university prep lab or in Haarmann

& Reimer's Holzminden factory would be sufficient for a five-year supply of perfume and soap for Houbigant's customers.

Another illustration that past volumes of aroma chemical consumption were nowhere near the volumes realized today is seen in the flavor and fragrance market of 1930. The total world supply of linalool was obtained from 70 Mtons/year of Bois de Rose oil, which could generate about 1,400 Mtons of fragrance concentrate. Today the world uses about 3,700 Mtons of linalool alone. Thus the flavor and fragrance market has grown, and the definition of "commercial" has changed.

By 1900, more than a dozen firms had commercially manufactured coumarin. The first U.S. manufacturer was Monsanto in about 1910, followed by Rhône-Poulenc (in Jersey City, New Jersey) in 1915, Dow in 1929 and Clemenson Chemical Co. in 1930 (bought out by Trubek in 1946).

In 1954, approximately 200 Mtons of coumarin was used in flavors and as a chrome plating brightener. That same year, based on some shoddy research, the FDA banned the use of coumarin in foodstuffs, classifying coumarin as a carcinogen. Some equally messed up reviews appeared in 1973. More reliable recent studies<sup>21</sup> have shown that coumarin is probably not a carcinogen in humans, and have led

to its classification as a Group 3 chemical with only limited toxicity. However, the coumarin controversy over the past 40 years has taken its toll. Coumarin has been approved by IFRA for use in fragrances,<sup>20</sup> but its use as a direct additive in foods and flavors is banned in the U.S., EEC, Japan and India, and in most other areas of the world its use in foods is controlled by a concentration limit. It is still used in tobacco flavors in Asia, but not in the U.S. or Europe. Its use in automobile chrome plating has been almost eliminated.

This coumarin controversy has inhibited coumarin's growth and reduced the number of world producers to only three firms. Its growth as a fragrance ingredient is less than the growth of other aroma chemicals that showed similar volume in 1955.

### World Consumption

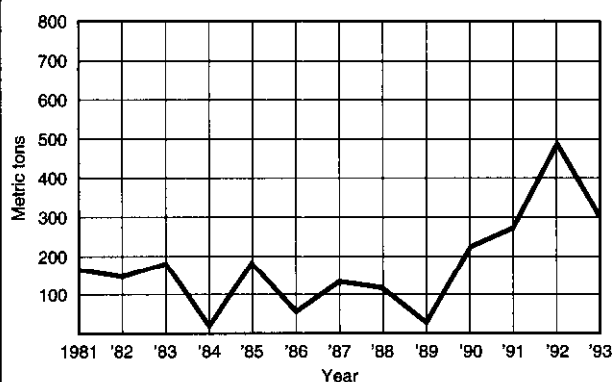
The coumarin consumed in 1995 will be all synthetic product except for minor, basically unmeasurable amounts consumed via essential oils and herbs. Almost all the synthetic coumarin will be used in fragrances, with a small amount used in tobacco flavors. Total world usage in 1995 is estimated to be 1,850 Mtons and breaks down as follows:

#### World consumption of coumarin in 1995 in Mtons

Fragrances	1,700
Flavors (includes tobacco)	100
Other	50
<b>Total</b>	<b>1,850</b>

#### Regional consumption in 1995 in Mtons

North America	500
Latin America	100
Europe - EEC	550
Europe - other	150
Japan	50
Asia	400
Africa and other	100
<b>Total</b>	<b>1,850</b>



**Figure 2. Coumarin imports into the United States in metric tons/year**

## Pricing

Coumarin prices have remained fairly steady at around \$7.00/lb over the last ten years, with the exception of a few spikes in the \$7.50-11.00 range that did not hold.

Imports from China have greatly influenced the world market because China exports more than half of its production. U.S. imports from China have varied between 12 and 500 Mtons per year over the last ten years and have been the deciding factor in the flat price curve.

## Imports

Figure 2 shows coumarin imports into the U.S. from 1981 to 1993. Almost all these imports are from China, a few stray lots are from France. Whenever coumarin prices rose in a year when Chinese imports were minimal, the next year saw increased imports and decreased prices. The world market for coumarin is so small that even 100 tons of excess product is sufficient to have a drastic downward effect upon prices.

Coumarin imports are dutied under TSUS 2932.21 at 20% ad valorem. However, imports from China, as long as it enjoys GSP status, bear no duty.

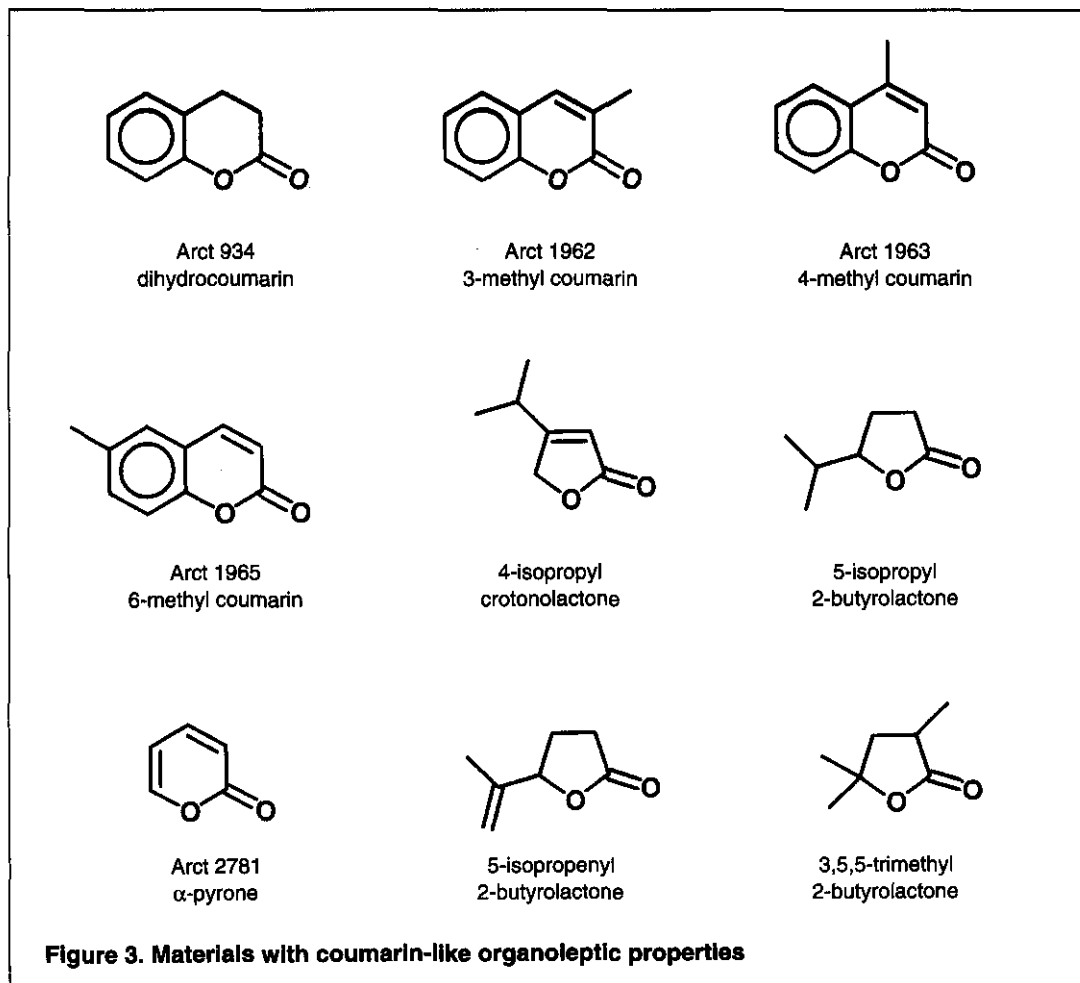
The recent International Trade Commission (ITC) findings of coumarin dumping by China in the U.S. and injury to Rhône-Poulenc, the sole U.S. coumarin producer, have

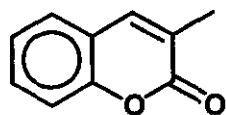
Table I. World producers of coumarin in 1995

Manufacturer	Estimated current production (Mtons)	Capacity (Mtons)
Rhône-Poulenc	850	1,500
China	850	1,000
Former USSR	150	200
<b>Total</b>	<b>1,850</b>	<b>2,700</b>

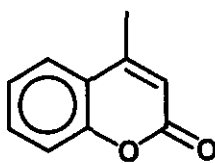
resulted in antidumping penalties of 15.04% (Jian Gsu Native manufacturing company in China), 50.35% (Tianjin Native manufacturing company in China), or 160.80% (any other company if the coumarin originally came from China), where these are ad valorem percentages of the amount of entered value of coumarin from the named manufacturers. Almost simultaneously with the ITC action, the European Trade Commission of the EEC found dumping and injury to Rhône-Poulenc from Chinese imports of coumarin into the European Economic Community. A punitive duty of approximately US\$4.50 was levied on future coumarin imports into the EEC.

Current supply and demand are well in balance, with

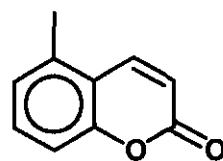




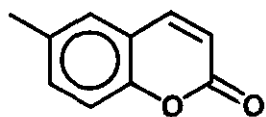
3-methyl coumarin  
Arct 1962  
coumrin-like



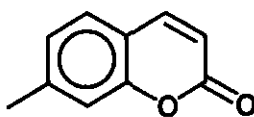
4-methyl coumarin  
Arct 1963  
coumarin-like



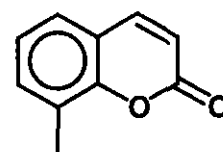
5-methyl coumarin  
Arct 1964  
herbaceous-woody



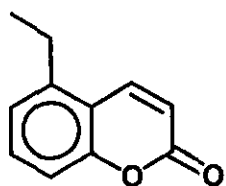
6-methyl coumarin  
Arct 1965  
coumarin-like



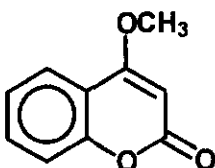
7-methyl coumarin  
Arct 1966  
musty leather



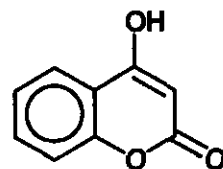
8-methyl coumarin  
Arct 1967  
woody-herbaceous



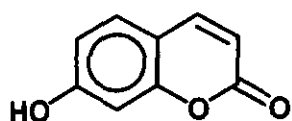
Arct 1194  
herbaceous, nutty



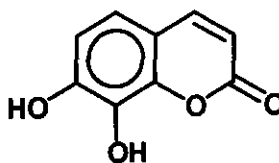
Arct 1871  
weak herbaceous



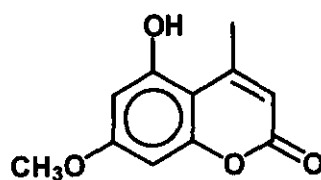
Arct 1739  
weak medicinal



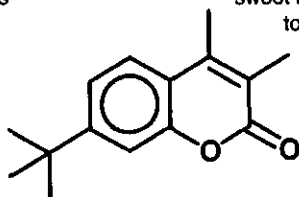
Umbelliferone  
Arct 3020  
sweet herbaceous  
coumarin



Arct 1073  
sweet herbaceous  
tobacco



Arct 1880  
dry musty herbaceous



Arct 997  
sweet musky nutty

Figure 4. Coumarin analogs

supply slightly in excess of demand. World demand is static, or growing at less than 1% per year. No future shortages are foreseen since existing world capacity can more than provide for the growth in demand over the next ten years, and China has recently added capacity. No new potential manufacturers are forecast to enter the market.

The major route used for the preparation of coumarin is the Perkin reaction, which employs salicylaldehyde as the critical intermediate. This method is used by both Rhône-Poulenc and China. The three known sources of coumarin, their capacity and current supply volumes are presented in Table I.

### Substitutes

Figure 3 shows materials that are reported to have coumarin-like organoleptic properties.<sup>17,18</sup>

### Analogs

Figure 4 shows analogs that appear in Arctander and present a good overview of the organoleptic impression of this group in general.

### Derivatives

Coumarin, itself, in moderate dosage, has no effect upon humans,<sup>19</sup> but is a narcotic to rabbits and a hypnotic and sedative for dogs and horses. Large doses will kill a dog or

a horse. The furanocoumarin, xanthotoxin, is extremely toxic to freshwater fish. Figure 5 shows the structures of coumarin derivatives.

The reports concerning the toxicity and carcinogenicity of coumarin were believed because so many derivatives of coumarin show physiological activity, some to the point of being commercial poisons.

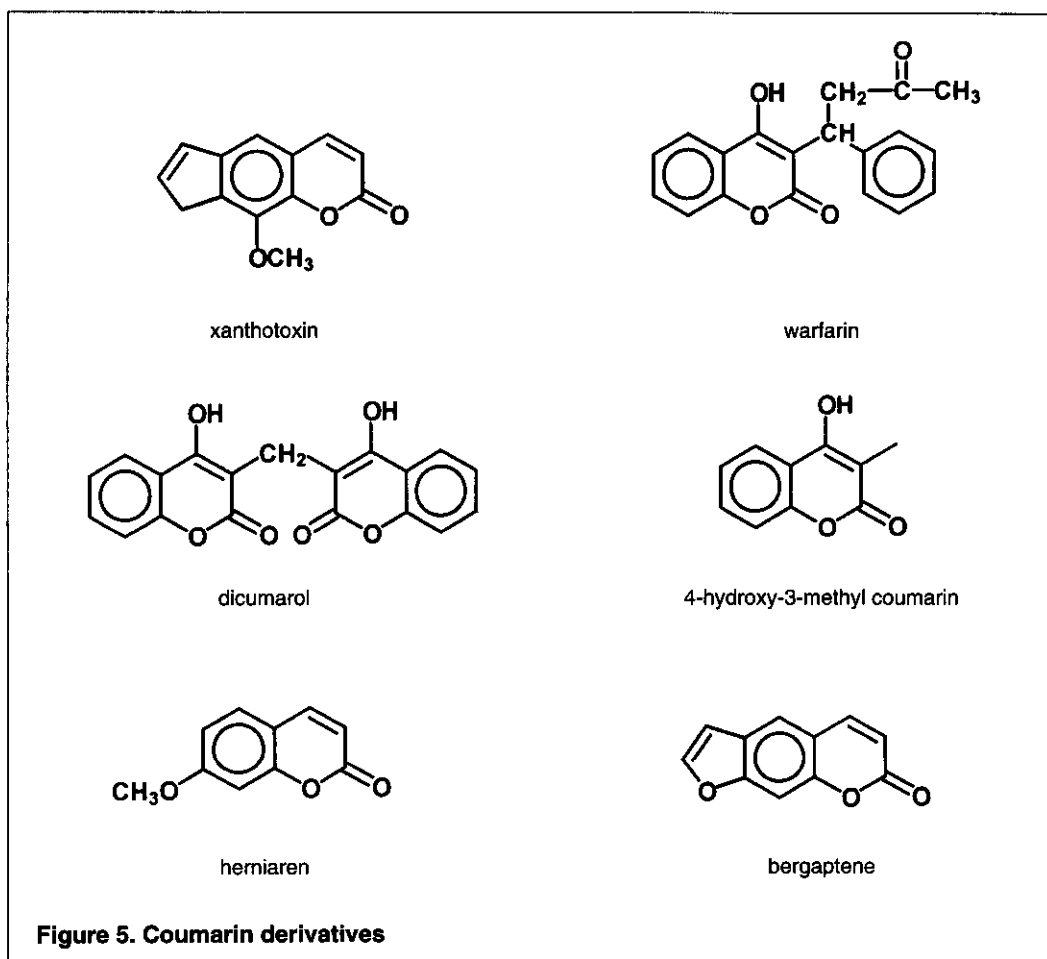
Warfarin is a widely used commercial rat poison which functions by inducing internal bleeding with repeated dosage. The asymmetric carbon containing the phenyl, acetyl and coumaryl group shows varied physiological activity as the levo antipode is 1,000 times more toxic than the dextro antipode. Various warfarin derivatives are either toxic and/or anticoagulants.

Dicumarol is a Vitamin K antagonist found in spoiled sweet clover (*Melilotus* species) that when eaten by cattle causes internal and external hemorrhaging and sudden death. It is used as an anticoagulant drug.

4-Hydroxy-3-methyl coumarin mimics Vitamin K and has the opposite effect of dicumarol in that it promotes the clotting of blood.

Herniaren is prohibited for use in fragrances by IFRA because it induces allergic and photoallergic reactions.

Bergaptene is one of a group of coumarin derivatives, furocoumarins, named psoralens, that show photo sensitization activity and phototoxicity. Because they have been



known to cause permanent discoloration of human skin, only bergaptene-free bergamot oil can be used in fragrances. (The bergaptene content of bergamot must be less than 5 ppm.)

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