An Aroma Chemical Profile

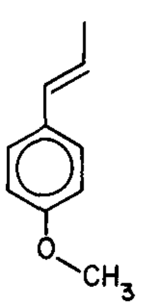
Anethole

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

Anethole's organoleptic profile is familiar to most of us as licorice. Until recently there were only negative reports of anethole's presence in licorice root, however one recent report[6] has identified its presence at trace levels (i.e., 1.8 x 10^{-4}% of the dry root). But it is added as a flavoring material. Its presence dominates the spices anise, star anise and fennel, which find wide use in all parts of the world. Thus, anethole's organoleptic impression is best defined by the terms *sweet, warm, anise-licorice*. The impression falls into the class "herbaceous" and defines the term anise in an aroma chemical sense. Yet, the term *anethole* is an anomaly, as it is derived from the Greek word *anethon*, meaning dill, a plant and oil in which anethole appears only as a minor constituent and in which it shades—but does not dominate—the character of the organoleptic impression.

Although anethole can be and sometimes is isolated from various anise oils in which it naturally occurs in high concentration (>90%), the current major commercial source of anethole is sulfate turpentine still bottoms. Anethole and its isomer estragol (methyl chavicol) are found only in minor concentrations in crude sulfate turpentine, thus its isolation would be impractical, if it were not for the huge volumes of turpentine crudes that are generated and processed for their other ingredients from U.S. southern pine trees. Anethole's isolation from this product stream places it as a by-product, which allows it to be priced at levels which vary considerably and often far below that level which would allow it to be produced by classical synthetic routes. This flexible price position has forced synthetic producers out of the market and prevents others from entering it.

Anethole



Mwt 148 $C_{10}H_{12}O$
FEMA-GRAS 2086
CAS 25679-28-1 cis- or (Z)-Anethole
CAS 4180-23-8 trans- or (E)-Anethole
CAS 104-46-1 Anethole, unspecified

Classification:
A phenyl methyl ether having a para propenyl group existing in cis- and trans- [or (Z)- and (E)-] forms.

Additional Names:[1-4]
trans-Anethole
iso-Estragole
para-Propenyl phenyl methyl ether
para-Propenyl anisole
1-Methoxy-4-(1-propenyl) benzene
Anise camphor
Monasirup

French: Anethol German: Anethol
Portugese: Anetol Spanish: Anetol

Physical Data:

Appearance:	colorless, white fused mass or clear colorless liquid (over 21°C)
Specific Gravity:	0.983-0.988 at 25°C
Congealing Point:	not lower than 20°C
Refractive Index:	1.5570-1.5610 at 20°C
Optical Rotation:	between -15° and +15°
Boiling Point:	231-237°C
Flash Point TCC:	213°F
Solubility:	<1% by weight in H_2O at 20°C; 33% in 90% ethanol; soluble in ether, benzene, aliphatic esters and alcohols, chlorinated hydrocarbons, ketones and aldehydes.

The melting point of trans-anethole has become a critical specification due to its depression by cis-anethole. cis-Anethole is about ten times more toxic than the trans isomer,[5] thus the melting point has been incorporated in the name of the commercially available product (i.e., Anethole 21/22° or Anethole 20/21°), in order to identify the concentration of cis isomer. A melting point of 20°C indicates a cis isomer content of about 3.5%.

 0272-2666/93/0005-0011$04.00/0—

Anethole occurs as both the cis- or (Z)- and trans- or (E)-isomers, the trans being more stable and hence found in the greatest concentration. Both isomers possess different organoleptic profiles and physical chemical properties, and have surprisingly different toxicity levels. The cis-isomer is 10-15 times more toxic than the more common trans isomer.

Isomer	LD_{50} rate	MP °C
trans- or (E)-anethole	900 mg/kg	21.4
cis- or (Z)-anethole	93 mg/kg	-22.5

These toxicity and organoleptic differences are reflected in the commercial specifications of the product found on the market and have been incorporated in the names of commercial products currently available: Anethole USP 20°/21°; Anethole USP 21°/22°; Anethole Extra 21.5°.

The number designation refers to the product's melting point or congealing point, thus guaranteeing it to be relatively free of the cis-isomer. Anethole USP 20°/21° has a melting point of 20-21°C and a cis-isomer content of less than .3%.

Trans-or (E)-anethole has a sweet, warm, herbaceous anise odor with a smooth clean top and end note. The taste is sweet, warm anise with no bitter tones. As most anethole present on the market today is isolated from crude sulfate turpentine bottoms, a great deal of processing effort goes into removing any sharp-bitter sulfur or burned phenolic notes that can pass through the system and display themselves in the finished product.

The major producers of finished anethole have mastered the technique of removing the undesired impurities, yet lots from lesser producers still appear on the market with enough impurities as to make the product unusable for most applications.

Natural Sources

Since anethole is produced via the shikimic acid pathway in plants, one would think that it would be found in most plant species. Unfortunately, anethole is produced from sedoheptulose via cinnamic aldehyde and then cinnamic alcohol by a mechanistic dead end that is found only in certain plant species (Figure 1).[7]

Thus, anethole is formed, but is not converted to other materials in the manner that cinnamyl alcohol is utilized as a mechanistic pathway step on the route to the formation of lignin. This mechanistic explanation covers the presence of anethole as it is found in fennel and anise, but may not explain its presence in sulfate turpentine bottoms. Anethole has not been noted in the normal oils of other pine species, but only in the sulfate turpentine resulting from the treatment of U.S. southern pine with heat and caustic conditions. The presence of both anethole and estragole in these turpentine bottoms may be a result of chemical cleavage of some ligneous material rather than a simple physical isolation of naturally occurring product.

The presence of both estragole and anethole in these bottoms and the ease of isomerization of estragole to anethole under the reaction conditions of the Kraft paper process, indicates that the anethole found there is a result of isomerization of estragole. However, even the presence of estragole as a naturally occurring isolate in this case is suspect. Nevertheless, the carbon-14 dating values for anethole and estragole produced via this process will indicate the product

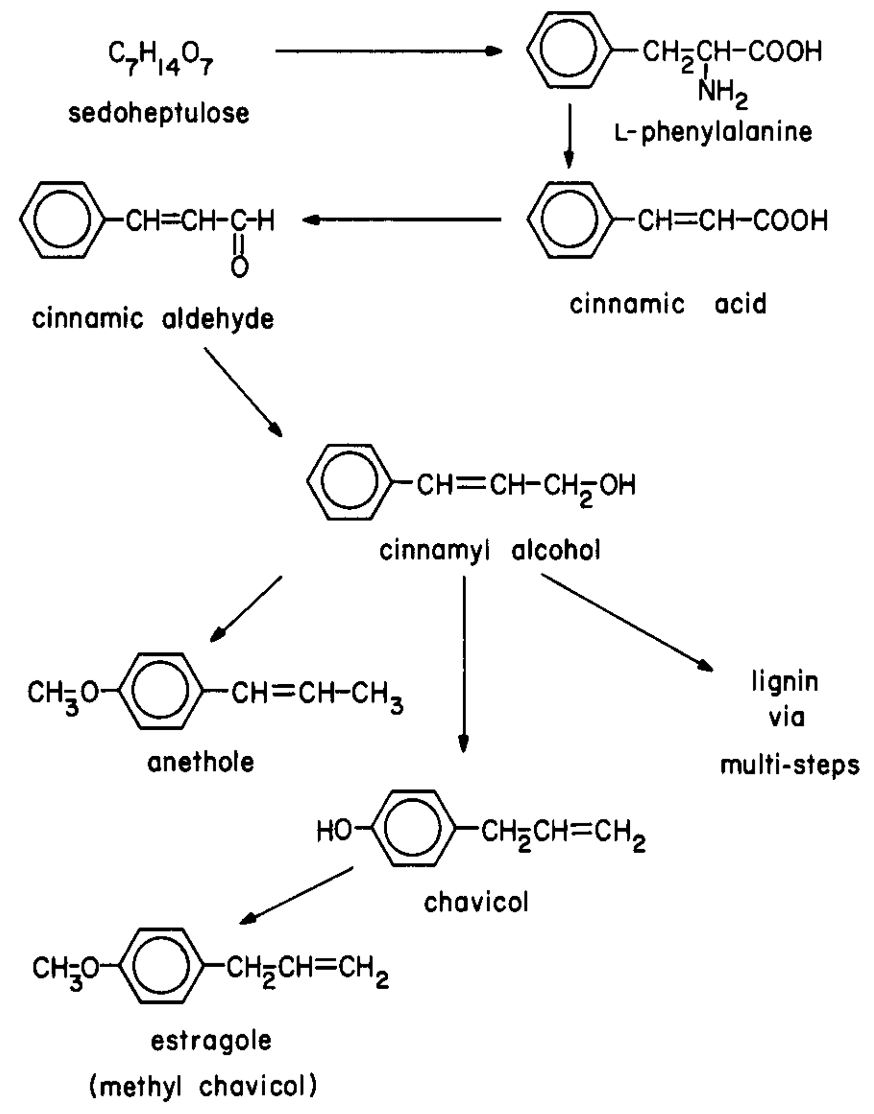


Figure 1. The shikimic pathway to anethole and estragole

as natural rather than synthetic.[5] In the past this has allowed finished sulfate turpentine anethole to be passed off as natural, when it is clearly a synthetic product. Recent use of carbon isotope ratio and hydrogen/deuterium/tritium isotope ratio methods have shown that having a reliable means of identifying sulfate turpentine-based anethole is a practical way to prevent this misrepresentation.[8]

Anethole has been reported in the following plants at the levels indicated:

Clausena anisata	74-90%
Heracleum lehmannianum	80
Magnolia salicifolia	73
Euxylophora paraenis	70
Backhousia anisata	60
Foeniculum panmosium	60
Pelea christopherensis	40
Ocimum menthae folium var. *anisata*	39
Piper betle	32
Aster jataricus	10

In only a few common plants is anethole found in more than trace amounts, and of the four most common species, the first three have been used in the past for the isolation of natural anethole.

Major Sources	% found	% Anethole
Anise seed oil	2-3	90-95
Star anise	2.5-3.5	85-90
Fennel seed	4-5	50-85
Tarragon	0.5-1.5	10

The total world production of the seeds (fruits) of these first three items would allow isolation of only 380 tons of natural anethole, if all the material currently available was dedicated to that purpose.

Such small volumes of anethole potentially available from natural sources serve to illustrate the key position played by sulfate turpentine-based synthetic anethole in the world market today.

Anethole has also been reported in trace amounts in the following essential oils and natural products:

basil	green tea leaves
caraway	lemon balm
coriander	mandarin peel
clove	rose
dill, Indian	

History

Anethole's development as a pure aroma chemical has been hindered by its organoleptic profile in the sense that it dominates the profiles of the three traditional sources for its isolation; anise, fennel and star anise. Prior to 1950, whenever the anethole nuance was demanded, it could be brought forth by the use of one of these essential oils or even the use of the basic spice (as is the case even today in much of the world). The use of the spice or essential oil, thus, met the needs of flavorists, perfumers and cooks until the recent isolations of anethole from turpentine bottoms.

Table I. 1992 anethole producers

	Crude	Finished
Acedesa, Spain		x
Arizona, USA	x	x
Bordas, Spain		x
DGF, Spain		x
Elpee, India		x
Formosa Perfume, Brazil		x
Fruitarom, Israel		x
Geroma, Brazil		x
Ghaziabad Aromatics, India		x
Glidco, USA	x	x
Haarmann & Reimer, Germany		x
Hercules, USA	x	x
Hindustan Chem & Allied, India		x
Quest, UK		x
Siva, India		x
Surya, India		x
Takasago, Japan		x
Toyotama, Japan		x
Union Camp-BBA, USA	x	x
Yasuhara, Japan	x	x

Human consumption of anethole via spices goes back to the dawn of history, with both Asian and European consumption documented prior to 900 B.C. In many cultures, anise and fennel provided the bases of folk medicines, used as carminatives to relieve stomach upsets. Even today, many herbal liquors reputed to be "good for the stomach" contain anethole from these spices, and the use of fennel oil in "Fenchel Honig" (Fennel Honey) is still recommended in Germany to cure infant colic (and it works!). Since anethole is the major ingredient in anise, star anise and fennel, and the use of these spices to ease stomach problems developed independently in many parts of the world, one can assume anethole was the key beneficial ingredient.

The distillation of essential oils has been traced as far back as about 3000 B.C. to the Indus Valley civilization in what is present-day Pakistan.[9] By the year 1500, a vibrant essential oil trade flourished in Europe and both anise and fennel seed oils were common items of commerce.[10] The early 1800s saw the development of fractional distillation and Dumas' isolation of anethole and proposed emperical formula. However, natural anethole was never a common aroma chemical until after 1950, as the traditional three oils provided the effect whenever it was needed in the flavor and fragrance industry.

Up until that time, the small amounts of anethole required by the food, flavor, fragrance and pharmaceutical industry were made available by fractional crystallization from anise or star anise oil.

What made anethole into a common pure aroma chemical was its identification in sulfate turpentine and the

Table II. Crude anethole suppliers, their estimated production for 1993, and their historic market share

	1993 Estimated Production in MTons	Historic Market Share in %
Arizona	100	8
Glidco	600	47
Hercules	200	16
Union Camp	370	29
Total	1270	100

Table III. World consumption of anethole in 1992

	World Consumption in MTons
Natural anethole (unisolated)	654
Essential oils	128
Synthetic anethole	1270
Total	2052

development of manufacturing aroma chemicals from turpentine sources pioneered by Glidden. In 1949, Glidden erected the first distillation unit dedicated to the separation of crude anethole from sulfate turpentine bottoms. These initial attempts to produce pure anethole met with mixed success because fractions rich in anethole and estragole could be isolated by fractional distillation but the various azeotropes (constant boiling mixtures with impurities anethole-caryophyllene or estragole-terpineol) frustrated U.S. producers' attempts to offer finished anethole. Although some U.S. producers of crude anethole manufactured and offered pure anethole prior to 1985, most found it more practical to sell their crude anethole/estragole fractions abroad, mainly to Spain. Thus, from 1950 until recently European manufacturers converted crude anethole to finished product, which was re-imported into the United States. Since 1985, U.S. producers of crude anethole have concentrated more on finishing their crude product in the U.S. to supply domestic needs and the importation of pure trans-anethole has nearly stopped. Still, large amounts of U.S. crude anethole/estragole fractions are being exported today for finishing outside the country, making the U.S. the major supplier to the world.

The availability of synthetic anethole from sulfate turpentine bottoms at relatively low costs has prevented the products' manufacture by direct synthesis from petrochemical feed stocks. In the 1970s, Haarmann and Reimer started up a synthetic trans-anethole unit in Germany, but shut it down after a few years of operation, as its volume oversupplied the market, causing prices to drop below Haarmann and Reimer's cost of production.

The most recent change in the anethole market is the growing interest in natural anethole for flavors. This trend will no doubt intensify and rekindle interest in finding new natural sources.

Current Producers

The producers of anethole fall into two major classes: those that are basic manufacturers of the crude product and supply some finished anethole, and those that manufacture finished anethole from purchased crude feed stocks. The major source of crude anethole is U.S. producers. Table I lists the major world suppliers/manufacturers of anethole—both crude and finished product.

The suppliers of the basic feed stock, crude anethole, for the production of finished anethole are relatively few compared to the plethora of firms offering the finished product.

Table II lists the main suppliers of crude anethole and their 1993 estimated production as well as historic market share.

Imports

Anethole falls in the TSUS Harmonized Tariff class 2909.30.20.008, which, although it can be dutied at 6.5% ad valorum, is allowed in duty-free from most producing countries enjoying GSP status.

World Consumption

For 1992, total world consumption of anethole in the form of spices, essential oils and synthetic product is estimated at 2052 MTons. This figure is based on averages, as the yearly production figures can vary as much as 10% from the average, due mainly to synthetic anethole production. The breakdown of anethole consumption is presented in Table III. The total anethole consumption figures include both isolated product and product that is consumed directly unisolated in the form of spice or as essential oils containing anethole.

Table IV presents a breakdown of the estimated anethole

Table IV. Anethole use in MTons by product area, estimated for 1992

	Oral Hygiene	Beverages	Confections	Baked Goods	Other	
Europe	200	220	80	50	30	
Asia	100	50	100	100	180	
North America	200	50	50	50	160	
Latin America	100	100	20	20	60	
Other	40	30	20	10	2	
	640	450	270	230	462	Total: 2052

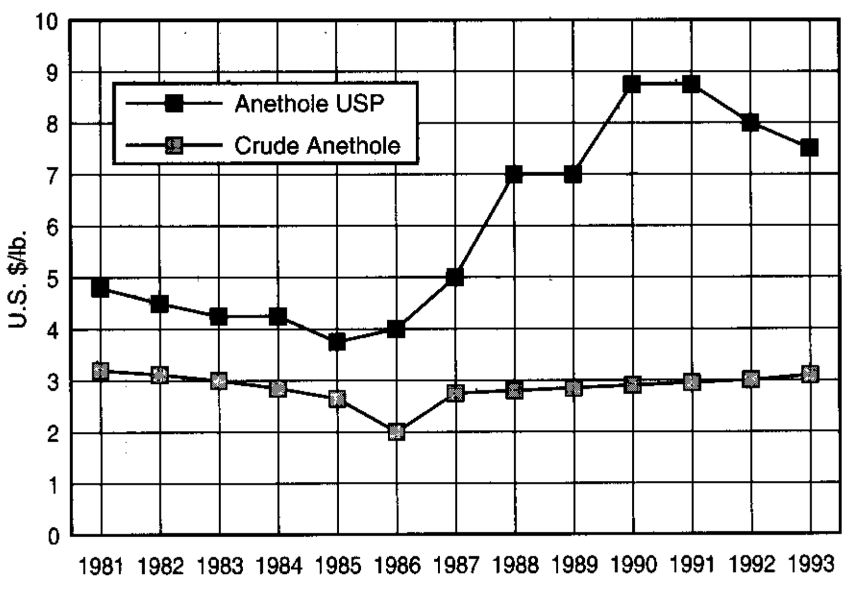
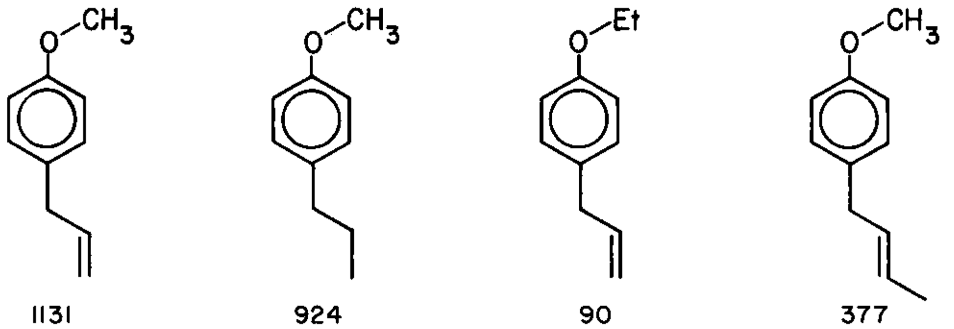


Figure 2. Anethole prices

usage from all sources (spices, essential oils and synthetics) in various end-use applications by world geographic areas. The large volume of usage in beverages, mainly alcoholic liquors and aperetif wines, is predominant in Europe, Latin America and parts of Asia. The single largest volume usage of isolated anethole is for oral hygiene products, such as toothpaste and mouthwash, where synthetic anethole is used for its sweet notes. These estimates are somewhat arbitrary, as it is difficult to closely estimate compounding usage for flavors versus consumption of consumer products manufactured locally or imported. Moreover, a fair amount of synthetic anethole is being marketed as natural, as it has been difficult until recently to differentiate between the isolate product from essential oils and the product resulting from sulfate turpentine sources.

Pricing

Anethole pricing has varied widely over the past twenty years (Table V). Prices, one would think, should reflect the availability of crude sulfate turpentine and hence crude anethole as the market is relatively inelastic with a growth rate of about 4% per year. Thus, during U.S. recessionary periods (1982) when the demand for paper products fell (sometimes as much as 20%), the availability of crude sulfate turpentine fell correspondingly and often to volumes below world demand. Thus, prices should rise. During periods of full pulp and paper mill capacity (1986-1989) the availability of crude sulfate turpentine increases, which should be



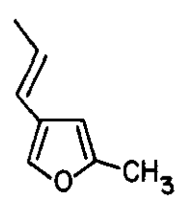
1131 — Estragole (Methyl chavicol)
924 — Dihydro anethole
90 — Allyl phenethole (Ethyl chavicol)
377 — β-Butenyl-p-methoxybenzene

Figure 3. Materials with organoleptic profiles resembling that of anethole (numbers refer to Arctander's work[2])

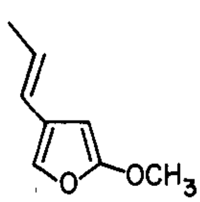
reflected by excess production and lower prices for crude and finished anethole. Between 1980 and 1990 it is estimated that U.S. crude sulfate turpentine availability increased by more than 20% due to heavy domestic demand for paper products, increased exports due to the lower dollar exchange rate, and pollution control systems which captured more volatile organics from the mills.

The graph (Figure 2) of anethole prices (both crude and finished product) does not reflect these market forces. Anethole's upper price limits are determined by the production cost of synthetic anethole from petrochemical feed stocks, but with the history of wide price variability (1970 to date) for the product, few synthetic chemical manufacturers would gamble on a production facility investment. This upper price level for finished anethole is currently estimated to be in the area of $8.00-9.00 per pound.

Thus, one must draw the conclusion that anethole price and availability are not feed-stock limited, but are based on a marketing decision aimed at optimizing sales revenue and maintaining fairly constant prices as reflected by anethole's recent price history. The supply of crude anethole from U.S. crude sulfate turpen-

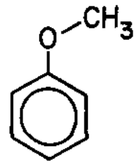


Methyl propenyl furan
I

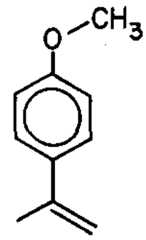


Methoxy propenyl furan
II

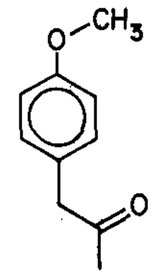
Figure 4. Materials that may have properties resembling those of anethole



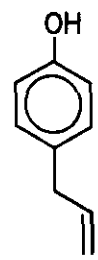
246
Anisole
harsh sweet anise



2644
p-Isopropenyl anisole
sweet anise-caraway

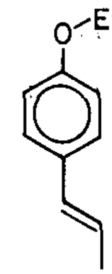


1883
p-Anisic ketone
hawthorn-anise

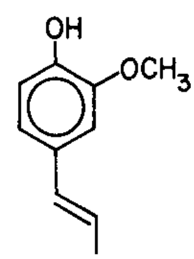


606
Chavicol
tarry phenolic

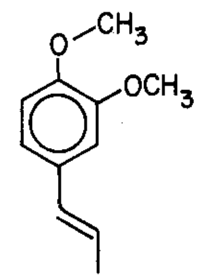
2650
p-Propenyl phenol
warm spicy



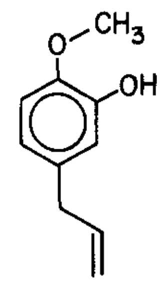
1688
Ethyl anethole
floral-herbaceous



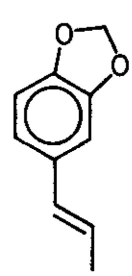
1370
Isoeugenol
clove



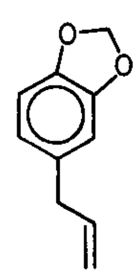
2027
Methyl isoeugenol
floral-carnation



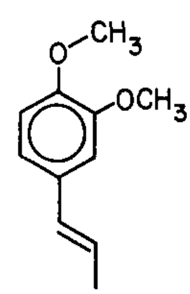
347
Betelphenol
sweet-smokey



2814
Isosafrole
sweet floral anise



2813
Safrole
sweet spicy



1866
Methoxy isochavibetol
vanilla-phenolic

Figure 5. Some analogues of anethole (numbers refer to Arctander's work[2])

tine at current mill capacity is estimated to be sufficient to supply about 1680 MTons/year or, at the current growth rate, enough synthetic anethole for world demand for the next ten years.

Substitutes and Derivatives

As with many aroma chemicals in wide use today, popularity reflects not only availability, but the reality that these materials are the best fit currently developed for the organoleptic profile demanded by the market. Therefore, no real good substitute for anethole is available—at least there is none that provides the same profile at a competitive price as the "real thing."

Figure 3 shows materials that have been reported to have anethole-like organoleptic profiles.

Anethole's basic structure and that of the other materials reported to have anise-fennel characteristics would lead one to speculate that the materials in Figure 4 may have anethole-like properties.

The key determinants of anethole's anise-like character seem to be an aromatic ring with a 1-2-propenyl group and methoxy group spaced as far apart as possible. The oxygen atom contained in the furan ring of compound I in Figure 4 may provide enough electron-rich polar influence to provide an anise character, although its benzene ring analogue has a gassy-aromatic hydrocarbon character.

Analogs

The presentation of analogs (Figure 5) in the case of anethole with its simple basic chemical structure borders on poetic license. Materials seemingly chemically close in structure show surprising variation in organoleptic impression and can vary far from the anethole accord.

References

Address correspondence to George S Clark, Commodity Services International, Inc, PO Box 1876, Easton, MD 21601 USA.

1. Anethol NF XVII Monograph, *The United States Pharmacopeia, National Formulary* (Jan 1, 1990) p 1900
2. Arctander, *Perfume and Flavor Chemicals* No 236 (1968)
3. *The Merck Index*, No 668, Rahway, New Jersey: Merck & Co, Inc (1983)
4. *The Givaudan Index*, New York: Givaudan Delawanna, Inc (1961) p 56
5. PAP Liddle and A Bossard, The analysis of anethole and anethole flavoured beverages by gas chromatography, *Proceedings of the Alko Symposium on Flavour Research of Alcoholic Beverages*, Helsinki (1984) pp 99-109
6. H Kameoka and K Nakai, Components of essential oil from the root of *Glycyrrhiza glabra, Nippon Nogei Kagaku Kaishi* **61**(9) 1119-1121 (1987)
7. U Senanayake and R Wijesekera, The volatiles of the cinnamonum species, *Proceedings of the ICEOFF 1989* **4** 103-126 (1989)
8. JA Buchel, Flavouring with essential oils - Importance to consumer and producer, *Commercial Papers of the Proceedings of the 11th CEOFF 1989* **6** 171-182 (1989)
9. P Rovesti, Distillation is 5000 years old, *Dragoco Report* **3** 59-62 (1977)
10. F Wells and M Billot, *Perfumery Technology*, 2nd ed, Ellis Horwood Ltd (1981) p 24