

1,3,5-Undecatriene and 2-Methoxy-3-isobutylpyrazine —Galbanum Green Notes

Chemistry and application in flavor and fragrance

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1,3,5-Undecatriene (FEMA# 3795, CAS#16356-11-9) (**F-1**) occurs naturally in apple, peach, Bartlett pear, pineapple, celery and parsley. It has a powerful, diffusive, green and characteristic galbanumlike odor and flavor, and it is applied in green fruit and herbal flavorings. It will give personality and lift to many fragrance types whenever a unique green note is desired.

2-Isobutyl-3-methoxypyrazine (FEMA# 3132, CAS# 24683-00-9) (**F-2**) occurs naturally in green bell pepper and petitgrain oil. It has a strong green note, characteristic of green bell pepper and green peas, and it is used in coffee and vegetable flavors, as well as in green-floral compounds such as petitgrain in fragrances.

Galbanum is an aromatic gum resin, the product of certain umbelliferous Persian plant species, chiefly *Ferula gummosa*, syn. *galbaniflua* and *Ferula rubricaulis*.¹ The characteristic harsh green odor of galbanum oil arises to a great extent from minor constituents, of which (3E,5Z)-undeca-1,3,5-triene (CAS# 19883-27-3) (**F-3**) and 2-methoxy-3-isobutyl-pyrazine are the most important.

The isomer (3E,5Z)-undeca-1,3,5-triene occurs naturally in apple, peach, Bartlett pear, pineapple, celery and parsley. It features the material's powerful, diffusive, green, characteristic, galbanumlike odor and flavor, and it can be applied in green fruit and herbal flavorings.^a

Additional isomers of undeca-1,3,5-triene are (Z,E)-1,3,5-undecatriene (CAS# 19883-27-3) and (Z,E)-1,3,5-undecatriene (CAS# 19883-27-3) (**F-4**). The isomers' mix has an oily, waxy, intensive green galbanumlike, slightly fruity odor.

(3E,5E)-1,3,5-Undecatriene (CAS# 19883-29-5) can be synthesized by performing the Wittig reaction of methylene triphenylphosphorane (CAS# 1099-45-2) with (2E,4E)-decadienal (FEMA# 3135, CAS# 246-668-9) to give the undecatriene with 90% yield (**F-5**).²

The 3E,5Z isomer can be prepared from hexyltriphenylphosphonium bromide (CAS# 4762-26-9) and (E)-2,4-pentadienal (CAS# 20432-40-0) with 67% yield, accompanied by the all-E isomer.³

The galbanumlike odor of another important perfumery ingredient—Dynascone^b (1-(5,5-dimethyl-1-

cyclohexenyl)pent-4-en-1-one (CAS# 56973-85-4) (**F-6**)—having a green, fruity, floral odor, is an extremely powerful and diffusive material that has an odor reminiscent of galbanum, with a pineapple and hyacinth character.

The complex galbanum odor blends with many different accords. Galbanum is one of the important components in *Vent Vert* (Balmain), giving it a green-floral accord. In *Chanel No. 19* (Chanel), galbanum shows its efficacy with floral and woody notes. In the development of synthetic galbanum odorants, galbanum is used in fragrances to impart fruity-green, especially pineapple notes, as shown by acetic acid, 2-(cyclohexyloxy)-, 2-propen-1-yl ester (CAS# 68901-15-5; Cyclogalbanat^c) (**F-7**).

The second green note molecule, 2-methoxy-3-isobutylpyrazine, can be prepared by a direct method by condensing 2-amino-4-methylpentanoic acid amide (CAS# 13079-20-4) with oxalic aldehyde (CAS# 144-62-7) (**F-8**).⁴

2-Methoxy-3-isobutylpyrazine is contained in grapes and red wine. From a comparison of the 2-methoxy-3-isobutylpyrazine concentrations of 50 red Bordeaux and Loire wines from different vintages and grape varieties (cabernet sauvignon, cabernet franc and merlot) with the intensity of the green bell pepper character as perceived on tasting, the threshold value was estimated to be 15 ng/L.

^c Cyclogalbanat is a trade name of Symrise.

Physical Data for 2-Methoxy-3-isobutylpyrazine

Appearance: Colorless clear liquid

Molecular weight: 166.2

Molecular formula: C₉H₁₄N₂O

Specific gravity: 0.9830–1.0030 (25°C)

Refractive index: 1.4870–1.4970 (20°C)

Boiling point: 214–215°C

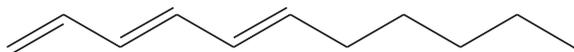
Flash point: 176°F (80°C)

Log P: 2.62 (estd.)

^a Some organoleptic information is taken from FRM 2001 *Database of Perfumery Materials & Performance*, Boelens Aroma Chemicals Information Services, The Netherlands.

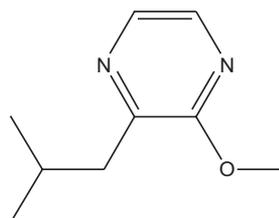
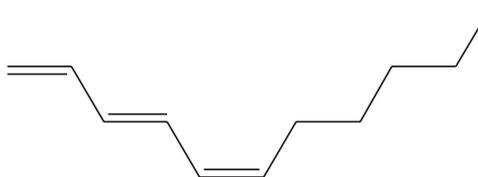
^b Dynascone is a trade name of Firmenich.



**1,3,5-Undecatriene****F-1**

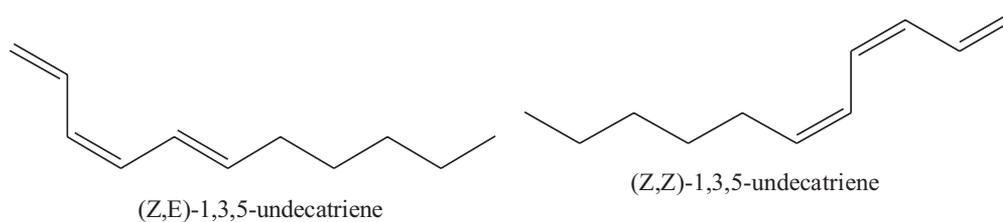
Physical Data for 1,3,5-Undecatriene

Appearance: Colorless clear oily liquid
Molecular weight: 150.3
Molecular formula: $C_{11}H_{18}$
Specific gravity: 0.7880–0.7960 (25°C)
Refractive index: 1.5100–1.5180 (20°C)
Boiling point: 280–285°C
Flash point: 176°F (80°C)
Log P: 5.05 (estd.)

2-Isobutyl-3-methoxypyrazine**F-2****(3E,5Z)-Undeca-1,3,5-triene****F-3****(3E,5Z)-undeca-1,3,5-triene**

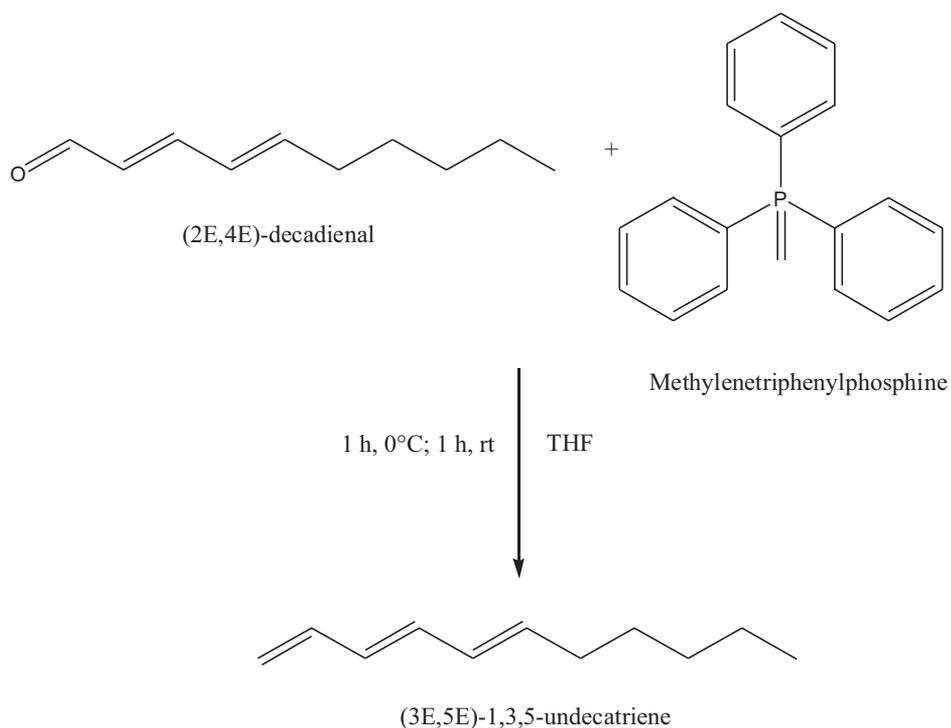
Additional isomers of undeca-1,3,5-triene

F-4



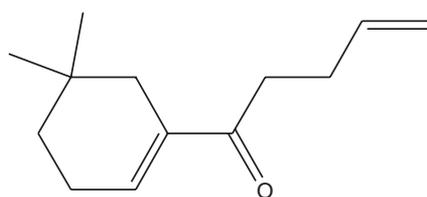
(3E,5E)-1,3,5-Undecatriene created from a Wittig reaction of methylene triphenylphosphane and (2E,4E)-decadienal

F-5



4-Penten-1-one, 1-(5,5-dimethyl-1-cyclohexen-1-yl)-

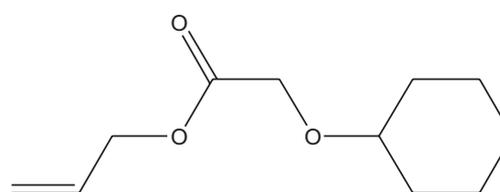
F-6



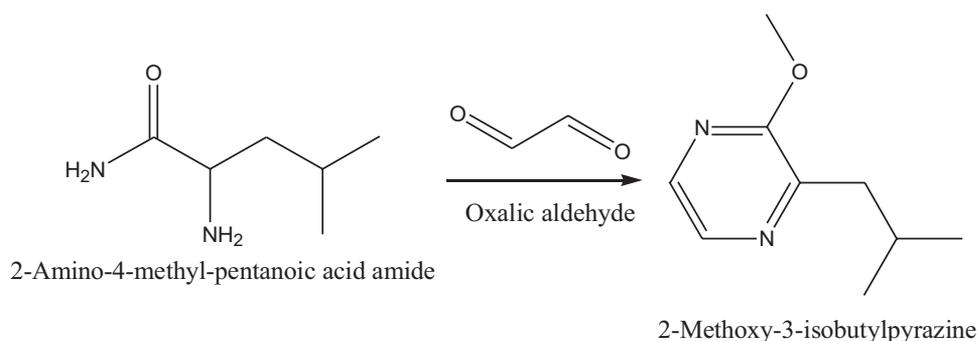
4-Penten-1-one, 1-(5,5-dimethyl-1-cyclohexen-1-yl)-

Acetic acid, 2-(cyclohexyloxy)-, 2-propen-1-yl ester

F-7



Acetic acid, 2-(cyclohexyloxy)-, 2-propen-1-yl ester



Analysis of the 2-methoxy-3-isobutylpyrazine concentrations of red Bordeaux wines showed cabernet wines were more commonly affected by this vegetative character.⁵

2-Isobutyl-3-methoxy-pyrazine also can be found within the volatile flavor components of baked potato flesh, and it is one of the more potent odorants in medium-roasted Arabica coffee, but it is also one of several musty, off-flavors in beer.^{6,7} Musty compounds can be introduced to beer via source water or raw materials, or, alternatively, may be produced within the brewery.⁸

On the other side, 2-methoxy-3-isobutylpyrazine can be used in green-type compounds for fragrances, as shown by the demonstration formula for a petitgrain base (**T-1**).⁹

References

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2. MJ Dabdoub, VB Dabdoub, ACM Baroni, GR Hurtado and SL Barbosa, *Tetrahedron Letters*, 51 (13) 1666–1670 (2010)
3. OA Garibyan, AL Ovanesyan, GM Makaryan and ZA Chobanyan, *Russian J of App Chem*, 81 (3) 455–458 (2008)
4. DA Gerritsma, ID Brindle, TRB Jones and A Capretta, *J Labelled Compd Radiopharm*, 46 (3) 243–253 (2003)
5. D Roujou de Boubee, C Van Leeuwen and D Dubourdiou, *J Agric Food Chem*, 48 (10) 4830–4834 (2000)
6. SC Duckham, AT Dodson, J Bakker and JM Ames, *Nahrung*, 45 (5) 317–323 (2001)
7. F Mayer, M Czerny and W Grosch, *Euro Food Res Tech*, 21 (4) 272–276 (2000)

Demonstration formula for a petitgrain base

T-1

| INGREDIENT | PARTS |
|---------------------------------|-------|
| Methyl anthranilate | 2 |
| Clary sage oil | 5 |
| Caryophyllene | 5 |
| Nerol | 8 |
| Neryl acetate | 10 |
| Citronellol | 15 |
| Orange terpenes | 25 |
| Terpenyl acetate | 30 |
| Geraniol | 40 |
| α-Pinene | 40 |
| Geranyl acetate | 60 |
| Terpineol | 100 |
| Linalool | 250 |
| Linalyl acetate | 400 |
| 2-Methoxy-3-isobutylpyrazine 1% | 10 |

8. M McGarrity, C McRoberts and M Fitzpatrick, *MBAA Tech Quarterly*, 40 (1) 44–47 (2003)
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