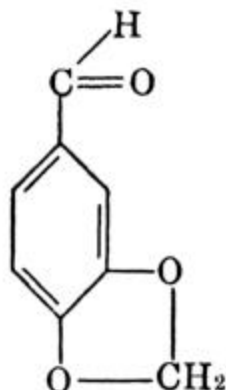


Piperonal

 $C_8H_6O_3$

Mol. Weight 150.13

3,4-Methylenedioxybenzaldehyde. Heliotropin



Occurrence.—It remains doubtful whether this aromatic aldehyde occurs in the beans (fruit) of various vanilla species, also whether the odor of heliotrope flowers is due to piperonal. Traces of piperonal have, however, been found in a few flower oils such as *Spiraea ulmaria* and *Robinia pseudacacia*. Recently reported in pha-chium oil by Ikeda et al.¹

Isolation.—Through the crystalline bisulfite compound which is sparingly soluble in water or alcohol.

Identification.—Piperonal can be characterized by the preparation of several derivatives:

- (1) Semicarbazone m. 234°, according to Wilson and Keenan.²
- (2) *p*-Nitrophenylhydrazone m. 201°, recorded by Quilico and Freri.³
- (3) 2,4-Dinitrophenylhydrazone m. 266° with decomposition (red crystals from glacial acetic acid), according to Campbell.⁴
- (4) Hydantoin m. 207°, by Henze and Speer.⁵

Gildemeister and Hoffmann⁶ recorded some additional derivatives and reactions useful for the identification of piperonal:

- (5) Monobromo compound m. 129°.
- (6) Mononitro compound m. 94.5°.
- (7) Thiosemicarbazone m. 185°.
- (8) *p*-Bromophenylhydrazone m. 155°.
- (9) Oxidation with aqueous potassium permanganate at 70°–80° yields piperonylic acid m. 227.5°–228°.
- (10) On addition of 40 per cent sodium hydroxide solution to an emulsion of piperonal, acetone and water, piperonalacetone m. 107°–108° is formed.

Properties.—Piperonal consists of colorless, shiny crystals m. 35°–36° according to Gildemeister and Hoffmann;⁷ 37° according to Othmer,⁸ and Fittig and Mielck.⁹ It possesses a sweet, flower-like odor, characteristic of heliotrope. Readily volatile with steam. The boiling point at 760 mm. is 263°. Gildemeister and Hoffmann¹⁰ also reported that piperonal is soluble in the usual organic solvents, sparingly soluble in cold water, more readily in hot water from which it can be recrystallized in the form of large crystals. Solu-

bility in water 2 : 1000 at 12°. Five parts of piperonal are soluble in 100 parts of 70 per cent alcohol at 10°.

When testing piperonal for the presence of impurities, it is advisable to determine its melting point and its behavior toward sodium bisulfite with which piperonal reacts readily.

On exposure to light and air, piperonal turns yellow and finally decomposes, being very slowly oxidized to piperonylic acid. It should, therefore, be stored in a cool, dark place and in airtight containers.

Use.—Piperonal is used widely in perfumery and for the scenting of cosmetics and soaps. Due to its distinct heliotrope odor it serves in lilac, carnation, sweet pea, and in fancy bouquets of all types. Piperonal blends well with coumarin and vanillin and imparts a lasting sweetness wherever used.

¹ *J. Chem. Soc. Japan* **61** (1940), 583. *Chem. Abstracts* **36** (1942), 6754.

² *J. Assocn. Official Agr. Chem.* **13** (1930), 390, 395.

³ *Gazz. chim. ital.* **58** (1928), 389.

⁴ *Analyst* **61** (1936), 392.

⁵ *J. Am. Chem. Soc.* **64** (1942), 522.

⁶ "Die Ätherischen Öle," 3d Ed., Vol. I, 539.

⁷ *Ibid.*

⁸ *Z. anorg. allgem. Chem.* **91** (1915), 212, 226, 242.

⁹ *Liebigs Ann.* **152** (1869), 38.

¹⁰ "Die Ätherischen Öle," 3d Ed., Vol. I, 539.

SUGGESTED ADDITIONAL LITERATURE

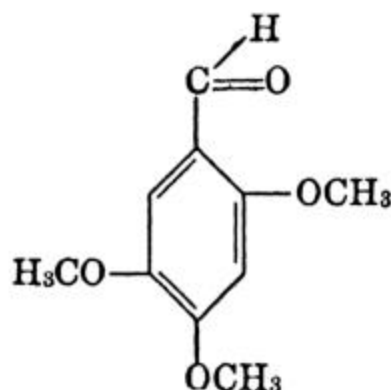
"Specifications and Standards" of the Essential Oil Association of the United States, January 10, 1947.

Asaronaldehyde

$C_{10}H_{12}O_4$

Mol. Weight 196.2

2,4,5-Trimethoxybenzaldehyde. Asarylaldehyde



Occurrence.—Gerö¹ found in the volatile oil derived from the roots of wild Hungarian hazelnut, *Asarum europaeum* L. (fam. *Aristolochiaceae*), an aldehyde, viz., asaronaldehyde, which, according to mixed melting point determination with an authentic sample, proved to be 2,4,5-trimethoxybenzaldehyde.