[CONTRIBUTION FROM THE LABORATORIES OF COMPAGNIE PARENTO, INC.]

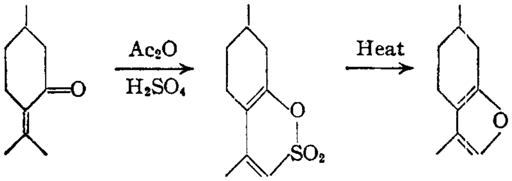
Occurrence of Menthofuran in Oil of Peppermint (Mentha piperita vulgaris S.)

BY PAUL Z. BEDOUKIAN

In 1904, Charabot[1] obtained from the flowering heads of the peppermint plant an oil which was found to have a rotation of +19° whereas the oil obtained from the whole plant was known to have a rotation of -19 to $-22°$. Further investigation of this oil by Carles[2] in 1929 showed that the positive rotation was due to the presence of an unidentified substance. This substance could not be isolated in the pure state but repeated distillations gave a fraction rich in the unknown substance with a rotation of +81°. Carles studied the properties of this substance and although he was unable to elucidate its structure his studies led him to believe it to be an oxide. The dextrorotatory substance was present in both French and Italian peppermint oils. It is noteworthy to mention a report of the occurrence of a dextrorotatory fraction in American peppermint oil which the investigator[3] attributed to the possible presence of *d*-menthone.

In 1934 Wienhaus and Dewein[4] deduced the structure of this dextro-rotatory compound to be tetrahydro-4,5,6,7-dimethyl-3,5-coumarane (menthofuran). Their deduction was based on experimental facts such as its complete reduction to *p*-menthane and oxidation to β-methyladipic acid. On hydrogenation it gave a product identical to the oxide derived from isopulegol which possessed an oxygen between the carbon atoms 3 and 9.

The syntheses of this unusual compound was successfully carried out by Treibs.[5] On treating pulegone (I) with cold acetic anhydride–sulfuric acid mixture by Reychler's method[6] Treibs obtained the cyclic ester of pulegenol sulfonic acid (II). When this compound was heated with an inert filler such as zinc oxide it lost one molecule of sulfur dioxide, giving a liquid of a composition $C_{10}H_{14}O$ (III).



I II III

The product was found to contain two double bonds which were conjugated, since the compound combined readily with maleic anhydride giving an addition product $C_{14}H_{16}O_4$. The conjugated double bonds were present in the furan ring because the vapor of menthofuran gave a deep red pine splinter reaction. Further evidence of the structure of synthetic menthofuran was obtained by degradation experiments.

The purpose of the present investigation was to establish conclusive proof of the presence of menthofuran in peppermint oil by direct comparison of the synthetic compound with the naturally occurring oxide.

In the examination of essential oils it is imperative to start with material of unquestionable purity. The peppermint oil investigated was obtained from plants grown in southern Ontario, the plants, *Mentha piperita vulgaris S.*, having been originally imported from Indiana. The writer was present during the harvesting and distillation period and acquired several drums of oil on the spot. The harvesting of the plant was begun as usual with the flowering of the plant and was continued for about two weeks. The fields were free from weeds and foreign plants. During the analysis of these oils which involved fractionation it was noted that a small fraction had a positive rotation, an unusual occurrence with peppermint oils. The properties of this oil were reported in a publication.[7] The dextro-rotatory fraction was separated and subjected to a study.[8] It was found impossible to obtain it in the pure state even after the removal by chemical means of menthone and menthol which have boiling points close to menthofuran. The purest fraction obtained had a rotation of +61° and exhibited properties similar to menthofuran as described in the literature. Its identity was established by the fact that its addition product with maleic anhydride did not give a depression in melting point when mixed with the addition product of synthetic menthofuran. The occurrence of menthofuran in oil of peppermint (*Mentha piperita vulgaris S.*) was thus definitely established.

Since menthofuran is present in relatively large quantities in the oil of flowering heads of *Mentha piperita vulgaris S.* and only in traces in oil of peppermint obtained from the whole plant, it is quite probable that the source of menthofuran in peppermint is the flower of the plant.

Menthofuran, in common with other furans, exhibits some interesting color reactions. On exposure to air both the natural and synthetic menthofuran turn purplish. This color, apparently due to the formation of an oxidation product, is completely removed by filtering the oil with magnesium carbonate powder. Menthofuran gives an intense blue–violet color on adding bro-

---

(1) Charabot, *Bull. soc. chim.*, **31**, 402 (1904).

(2) Carles, *Parf. Moderne*, **22**, 615 (1929).

(3) Gordon, *Am. J. Pharm.*, **99**, 524 (1927)

(4) Wienhaus and Dewein, *Z. angew. Chem.*, **47**, 415 (1934).

(5) Treibs, *Ber.*, **70B**, 85 (1937).

(6) Reychler, *Bull. soc. chim.*, **19**, 129 (1898).

(7) Bedoukian, *Am. Perfumer*, **46**, No. 2, 59 (1944).

(8) Part of this work was carried out in the laboratories of W. J. Bush & Co., Ltd., Montreal, Canada.

mine to its solution of carbon tetrachloride. This reaction recalls the behavior of azulenes. Similar color reactions of many essential oils may be due to the presence of such compounds of unknown structure.

Experimental

Separation of Natural Menthofuran.—The fraction of peppermint oil possessing a slight dextro-rotation was subjected to several fractionations and the fractions having a rotation of +15 to +20° were collected. The menthone present in these fractions was removed by means of semicarbazide hydrochloride. On fractionation the unreacted oil gave a product having a rotation of +61°, $d^{20}{}_{25}$ 0.930, $n^{25}{}_D$ 1.4657, b. p. (17 mm.) 92–94°. Carles[2] obtained a purer sample of natural menthofuran with the following constants: rot. +81°, b. p. (20 mm.) 95°, d^{15} 0.965, $n^{20}{}_D$ 1.4807.

Maleic Anhydride Addition Product of Natural Menthofuran.—The above impure menthofuran (5 g.) was added to 15 ml. of benzene containing 5 g. of maleic anhydride. There was a noticeable rise in temperature and the mixture was allowed to stand for two hours. The crystals obtained after several recrystallizations from benzene had a m. p. of 133–133.5°. The mixed m. p. with the synthetic product showed no depression (m. p. 133°).

Preparation of Pulegenol Sulfonic Ester.—Oil of pennyroyal (100 g.) was fractionated and the fraction having a b. p. of 100–101° (17 mm.), rot. +21.50, $d^{25}{}_{25}$ 0.939, $n^{20}{}_D$ 1.4850, was taken as pure pulegone. Forty grams of pulegone was treated with 80 g. of an ice cold mixture of 2 moles of acetic anhydride and 1 mole of sulfuric acid. The temperature rose to 25° and the mixture was allowed to stand for two hours. The crystals obtained were filtered, washed and recrystallized from methyl alcohol, m. p. 86°. Treibs reports m. p. 85° for pulegenol sulfonic acid cyclic ester.

Formation of Menthofuran.—The above product (20 g.) was mixed with 20 g. of zinc oxide and heated at atmospheric pressure. When the oil-bath reached 280–290° strong fumes of sulfur dioxide came off followed by an oil of bluish color. The oil (13 g.) was first washed with water, then with a 5% solution of sodium carbonate, redistilled and the fraction (8 g.) of b. p. 205–206°, rot. +92° $n^{20}{}_D$ 1.4855, $d^{25}{}_{25}$ 0.966, was taken as menthofuran. It was a colorless oil which turned purplish on exposure to air. Treibs gives the following constants for synthetic menthofuran: b. p. 80° (18 mm.), d^{15} 0.972, n_D 1.4890, rot. +92°.

Maleic Anhydride Addition Product.—The same procedure was followed as with natural menthofuran. The maleic anhydride addition product had a m. p. of 133–133.5°. Treibs reports 138° for the m. p. of the addition product of menthofuran. Both the natural and synthetic menthofuran exhibited a greenish coloration and fluorescence in benzene solution although the crystals themselves were colorless.

Summary

A dextro-rotatory substance occurring in oil of peppermint (*Mentha piperita vulgaris S.*) was shown to be menthofuran (tetrahydro-4,5,6,7-dimethyl-3,6-coumarane). Its identity was established by the fact that its maleic anhydride addition product did not give a depression in m. p. when mixed with the maleic anhydride addition product of synthetic menthofuran.

Croton-on-Hudson, N. Y.

Received September 29, 1947

[Contribution from the Purdue Research Foundation and the Department of Chemistry of Purdue University]

Monomers and Polymers. II. α-Methylstyrenes and the Steric Hindrance of *ortho*-Substituents[1]

By G. Bryant Bachman and R. W. Finholt[2]

Although styrene (S) itself polymerizes readily in the presence of peroxides, α-methylstyrene (AMS) resists polymerization with peroxides and forms high polymers only in conjunction with other vinyl compounds.[2a] This is in part advantageous since the AMS may be stored even in the presence of air without loss (except by partial oxidation to acetophenone), and may be recovered from reaction mixtures with ease. The copolymers of AMS do not appear to differ markedly in physical properties from the analogous copolymers of S.

In undertaking a study of synthetic rubbers prepared by copolymerizing substituted α-methylstyrenes with butadiene we soon became aware of the importance of the relative positions of the substituent groups. Thus, 3,4-dichloro-AMS gave good rubbers with butadiene while 2,4-dichloro-AMS did not copolymerize. Construction of molecular models showed that the isopropenyl group is not free to rotate through 360° in the 2,4-isomer because of the hindering effect of the *ortho* chlorine atom. Such hindrance is not apparent in the S series, and there are numerous references in the literature to the polymerization of ortho substituted S's.[3] Models of the polymers of 2-chloro-AMS show that the phenyl groups are forced to lie at right angles to the direction of prop-

---

(1) From the Ph.D. thesis of R. W. Finholt, Purdue University, June, 1947.

(2) Present address: Department of Chemistry, Union College, Schenectady, New York.

(2a) Note, however, that acid and ionic catalysts cause polymerization of α-methylstyrenes. Staudinger and Breusch, *Ber.*, **62**, 442 (1929); Bergmann, Tanbadel and Weiss, *Ber.*, **64**, 1493 (1931); Hershberger, Reid and Heiligmann, *Ind. Eng. Chem.*, **37**, 1073 (1945).

(3) *o*-F-S, Brooks, This Journal, **66**, 1295 (1944), and private communication. 2-CH$_3$O-S, Walling and Wolfstirn, *ibid.*, **69**, 852 (1947), and private communication; Pschorr and Einbeck, *Ber.*, **38**, 2076 (1905); Klages and Eppelsheim, *ibid.*, **36**, 3590 (1903). 2,3-, 2,4-, 2,5- and 2,6-diCl-S's, British Patent 564,828 (Oct. 16, 1944); Marvel, Overberger, Allen, Johnston, Saunders and Young, This Journal, **68**, 861 (1946); Michalek and Clark, *Chem. Eng. News*, **22**, 1559 (1944). 2-CH$_3$-S, v. Auwers, *Ann.*, **413**, 295 (1917). 2,4-diCH$_3$ and 2,5-diCH$_3$-S's, Marvel, Saunders and Overberger, This Journal, **68**, 1085 (1946). 2-OH-S, Fries and Fickewirth, *Ber.*, **41**, 369 (1908). 2,4-di(OH)-S, Flood and Nieuwland, This Journal, **50**, 2568 (1918); etc.