complexing of the cobalt in vitamin B_{12} have been substantiated under considerably more rigorous conditions.

TABLE I

DISTRIBUTION OF RADIOACTIVITY DURING SEPARATION PROCEDURE

Fractionation step	$Co^{60}SO_4$-control Butanol counts/min.	$Co^{60}SO_4$-control $(NH_4)_2$-SO_4 counts/min.	B_{12}–Co^{60}, pH 2 Butanol counts/min.	B_{12}–Co^{60}, pH 2 $(NH_4)_2$-SO_4 counts/min.	B_{12}–Co^{60}, pH 7 Butanol counts/min.	B_{12}–Co^{60}, pH 7 $(NH_4)_2$-SO_4 counts/min.
1	49	3400	2400	30,000	2350	30,000
2	1	30	75	2,100	80	2,260
3			4	55	2	60

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The Isolation of Metanethole from the Sponge, *Spheciospongia Vesparia*[1]

BY WERNER BERGMANN AND WILLIAM J. MCALEER[2]

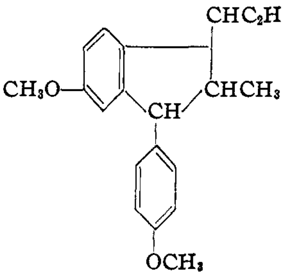
The odor of the majority of species of fresh sponges is not unpleasant, as is generally believed, but often rather aromatic and reminiscent of anise oil and similar products. The first clue to the probable nature of these odoriferous products was secured during a systematic fractionation of the unsaponifiable matter of the sponge, *Spheciospongia vesparia*.[2] In the present work, there was isolated from a fraction, consisting chiefly of hydrocarbons, a small amount of a nicely crystalline material of m.p. 135° and the empirical formula $C_{20}H_{24}O_2$. The compound failed to react positively with reagents for hydroxyl and carbonyl groups, and the absence of such groups was also noticed in its infrared absorption spectrum. The latter, however, showed that the two oxygen atoms were present as methoxyl groups. This was verified by a methoxyl determination according to Zeisel. The presence in the compound of two isolated aromatic rings was suggested by the low hydrogen content and the ultraviolet absorption spectrum. The compound reacted readily with bromine under evolution of hydrogen bromide to afford a nicely crystalline dibromide, $C_{20}H_{22}O_2Br_2$, m.p. 138°. It was also easily nitrated to a dinitroderivative, $C_{20}H_{22}O_6N_2$, m.p. 190°.

The properties of this sponge product were found to be in excellent agreement with those of metanethole (III), the dimerization product of anethole (I). The structure of metanethole, first proposed by Baker and Enderby[3] and supported by Müller and Richl[4] has recently been substantiated through the work of Doering and Berson[5] on the analogous di-isohomoeugenol.

Convincing proof for the identity of the sponge product with metanethole was established by direct comparison of the two compounds. Metanethole was prepared from *p*-methoxy-α-methylcinnamic acid according to Baker and Enderby.[3] The physical properties of the two products, including their absorption spectra, and their reactions with bromine and nitric acid which afford characteristic derivatives, were identical.

I, anethole

II, methylchavicol



III, metanethole

Like the synthetic material, the sponge product is optically inactive. This lack of activity in spite of the presence of three asymmetric carbon atoms suggests that the sponge product is an artifact. Its immediate precursor was in all probability anethole (I), a constituent of many essential oils, such as anise oil, in which upon long standing it dimerizes to give metanethole.[6] The possibility, however, is not excluded that the material present in fresh sponges is methylchavicol (II) rather than anethole. While it is true that methylchavicol does not readily dimerize to metanethole,[7] it will rearrange to anethole in an alkaline medium. It is not inconceivable that such rearrangement has taken place during the saponification of the original fatty extract of the sponge. The results of the present study therefore indicate that the odor of many sponges is due to the presence of small amounts of anethole, methylchavicol or other related substances. Such compounds which are not uncommon in many plants do not appear to have previously been observed in animals.

Experimental

All melting points are corrected.

The unsaponifiable matter of the sponge, *Spheciospongia vesparia*,[2] from which the bulk of the sterols had been removed by crystallization, was rapidly distilled from a small retort at about 0.02 mm. pressure. The fraction boiling below 230° was dissolved in hot acetone. Upon cooling, the solution deposited a small amount of a solid hydrocarbon mixture consisting chiefly of heptacosane. The mother liquor was then evaporated to dryness, and the residue (15 g.) was dissolved in hexane (50 ml.). The solution was then passed through a column of alumina, and the chromatogram was developed first with hexane and subsequently with hexane containing 20% of benzene, when four distinct zones appeared. The eluate containing the fastest moving zone upon evaporation afforded a yellowish oil (1.5 g.) interspersed with crystalline material. The latter (100 mg.) was readily separated from the oil by several recrystallizations from acetone. It melted at 135° and gave no depression of the melting point when mixed with synthetic metanethole.[3]

Anal. Calcd. for $C_{20}H_{24}O_2$: C, 81.05; H, 8.15; CH_3O, 20.9. Found: C, 81.16; H, 8.70; CH_3O, 20.6.

Dibromometanethole.—About 10 mg. of the sponge product was treated with 1 ml. of 10% solution of bromine in glacial acetic acid. Solution took place rapidly with the evolution of hydrogen bromide. After standing overnight, the crystalline dibromide was collected, washed with acetic acid and acetone, and recrystallized from acetone; m.p.

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(1) Contributions to the study of marine products. XXIX.

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138°. It did not give a depression of the melting point when mixed with authentic material.[3]

Anal. Calcd. for $C_{20}H_{22}O_2Br_2$: Br, 35.2. Found: Br, 35.5.

Dinitrometanethole.—About 10 mg. of the sponge product was dissolved in 2 ml. of hot glacial acetic acid, and the solution cooled rapidly to obtain a fine suspension of crystals. Addition of a few drops of concentrated nitric acid brought about a gradual disappearance of the suspended material, and upon cooling crystallization of the nitroderivative took place. It was collected, washed with acetic acid and recrystallized from ethanol; m.p. 190°. It did not give a depression of the melting point when mixed with authentic material.[3]

Anal. Calcd. for $C_{22}H_{22}O_6N_2$: N, 7.25. Found: N, 7.41.

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The Succinoylation of the Naphthols[1]

BY ERNST BERLINER, SHIRLEY B. DANIELS AND ALINA SURMACKA[2]

Although various phenols have been converted into the corresponding substituted β-benzoylpropionic acids with succinic anhydride and aluminum chloride,[3] the only reference to the succinoylation of the naphthols is an unsuccessful attempt with α-naphthol using either aluminum chloride or zinc chloride in tetrachloroethane or nitrobenzene solution.[4] Actually, both naphthols can be succinoylated, although the yields of keto acids are very small.

β-Naphthol, which was studied in greater detail, forms predominantly β-(2-hydroxy-1-naphthoyl)-propionic acid in refluxing benzene as well as in tetrachloroethane on the steam-bath. The acid was identified by converting it into the known methyl ether.[5] Between 60 and 70° in benzene solution there is obtained, in addition to the 1-acid, β-(6-hydroxy-2-naphthoyl)-propionic acid, and in tetrachloroethane at the same temperature β-(7-hydroxy-1-naphthoyl)-propionic acid. In carbon disulfide the yield of the 1-acid is very small, and an unidentified compound, melting at 146.5–147.5° is also formed. The formation of the 1-, 6- and 8-acid is anticipated in electrophilic substitution of β-naphthol. It was not ascertained whether the isomeric acids were obtained by direct substitution, or by a Fries rearrangement, as has been suggested for the succinoylation of phenols.[6] When the reaction in benzene was carried out in the presence of three equivalents of aluminum chloride, instead of the usual two, the only product isolated was β-benzoylpropionic acid. The complex between β-naphthol and aluminum chloride is therefore less susceptible to electrophilic attack than benzene.[7]

In boiling benzene or in tetrachloroethane at 100° α-naphthol is converted into β-(1-hydroxy-4-naphthoyl)-propionic acid, which forms the known β-(1-methoxy-4-naphthoyl)-propionic acid on methylation.[8] At 80° in tetrachloroethane an isomeric acid is obtained which gives a blue coloration with ferric chloride.[9]

Experimental

Succinoylation of β-Naphthol.—A mixture of 18 g. (0.12 mole) of β-naphthol, 10 g. (0.1 mole) of succinic anhydride and 26 g. (0.2 mole) of aluminum chloride was refluxed in 80 ml. of dry, thiophene-free benzene for one hour. The reaction mixture was worked up as usual,[3] and the oil (6.2 g.), which separated after acidifying the carbonate solution, was allowed to solidify. It was extracted with hot benzene and material melting between 200 and 230° was left behind. On addition of ligroin the benzene extract deposited 3.2 g. (13%) of β-(2-hydroxy-1-naphthoyl)-propionic acid which, after several recrystallizations from benzene–ligroin, formed almost colorless plates melting at 112.8–113.5°.[10] Crystallized from 50% methanol the acid melts at 118.3–118.8°.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 68.94; H, 5.13.

The acid was converted into the methyl ether (m.p. 136.7–138.2°) which gave no depression of the melting point when mixed with an authentic sample.[5] The above run was repeated with the same amounts of reagents, but the temperature was kept between 60 and 70°. The 1-acid was extracted with benzene, and the remainder was recrystallized from 50% methanol. The acid thus obtained melted at 230.1–230.7°. The values reported for β-(6-hydroxy-2-naphthoyl)-propionic acid are 229–231°[11] and 235°.[12] When the run was repeated with three equivalents of aluminum chloride the only acid isolated was β-benzoylpropionic acid (m.p. and mixed m.p.).

A mixture of 0.06 mole of β-naphthol, 0.1 mole of succinic anhydride and 0.3 mole of aluminum chloride was heated on the steam-bath in tetrachloroethane (100 ml.) solution. After two hours the reaction mixture was worked up as usual. The 1-acid was formed in an 11% yield.

A run with the same amounts of reagents was conducted at 60–70°. The mixture of acids was dissolved in hot benzene, and the benzene solution slowly deposited 0.4 g. (2.7%) of β-(7-hydroxy-1-naphthoyl)-propionic acid, which after two crystallizations from 50% methanol formed long, white needles melting at 179.2–179.4°.

Anal. Calcd. for $C_{14}H_{12}O_4$: C, 68.84; H, 4.95. Found: C, 69.00; H, 5.26.

The methyl ether of this acid, recrystallized from 50% methanol, melts at 145.6–146°. The value reported for β-(7-methoxy-1-naphthoyl)-propionic acid is 145–146°.[13] The benzene filtrate, after concentration and addition of ligroin, deposited 1.7 g. (11%) of the 1-acid.

In carbon disulfide only a small amount of the 1-acid was obtained in pure form. The remainder was a mixture which melted at first at 205–210°, but from which, after several crystallizations from 50% methanol, an apparently pure compound, melting at 146.5–147.5°, was isolated. The latter compound was not further investigated.

Succinoylation of α-Naphthol.—A run conducted on one-tenth of a mole of each α-naphthol and succinic anhydride and twice this amount of aluminum chloride in 100 ml. of boiling benzene afforded 1.5 g. (6.1%) of β-(1-hydroxy-4-

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[1] From the M.A. thesis of S. B. Daniels (1950) and the Senior Honors thesis of A. Surmacka, 1948.

[2] Mrs. Alina S. Szczesniak, Massachusetts Institute of Technology, Cambridge, Mass.

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[7] For a similar case see ref. 6.

[8] L. F. Fieser and E. B. Hershberg, THIS JOURNAL, **58**, 2314 (1936).

[9] The syntheses of β-(1-hydroxy-4-naphthoyl)-propionic acid (m.p. 235°, dec.) and of β-(2-hydroxy-1-naphthoyl)-propionic acid (m.p. 116°) by demethylation of the corresponding methoxy acids have in the meantime been reported (R. B. Burtner and J. M. Brown, THIS JOURNAL, **73**, 897 (1951)). The authors also report the synthesis of β-(1-hydroxy-2-naphthoyl)-propionic acid (m.p. 106–108°), but no structure proof is given.

[10] All melting points are corrected.

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