Tetrahedron Letters No.25, pp. 2971-2974, 1968. Pergamon Press. Printed in Great Britain.

GEOSMIN, FROM MICROORGANISMS, IS TRANS-1,10-DIMETHYL-TRANS-9-DECALOL

Nancy N. Gerber

Institute of Microbiology, Rutgers, The State University,
New Brunswick, New Jersey 08903

(Received in USA 19 February 1968; received in UK for publication 25 March 1968)

Microorganisms produce many volatile substances with strong odors. Two of the most important odors could be described as "earthy" and "musty." When such odors are imparted to foods and water supplies actinomycetes are blamed for the unpleasantness (1). Recently substances have been isolated from cultures of actinomycetes which can be held responsible for these odors.

Geosmin (2), $C_{12}H_{22}O$, is a neutral oil with an earthy odor at extremely high dilution which has been isolated from seventeen actinomycete strains (mostly streptomycetes) and one blue-green alga (3). Mucidone (4), $C_{12}H_{18}O_2$ was reported (5) to have a musty odor and taste and was produced by an actinomycete isolated from the Cedar River during an episode of severe mustiness (6). Through the kindness of Dr. A. A. Rosen these two substances were compared in his laboratories and found to be different in type of odor, threshhold odor number and gas chromatography (GC) retention time.

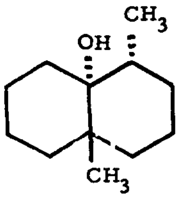
Pure geosmin, neat, does show an O-H band in the infrared (IR) which had not been observed earlier in carbon tetrachloride solution (2) or potassium bromide disk (3). The nmr spectrum on a larger sample clearly showed the presence of only two methyl groups on saturated carbons, a doublet centered at 0.75δ and a singlet at 0.99δ (7) not three as previously suggested (2). Geosmin with acid gives argosmin, $C_{12}H_{20}$ a neutral oil with no odor. However, on an extremely sensitive GC argosmin was shown to be a mixture of five substances (8). The three main peaks were in the olefin range, as judged by retention time, and were not completely resolved. All three olefins were inert toward mercuric acetate in methanol (9) under conditions where β pinene and anethole reacted readily. This indicates that all three olefins were highly substituted; they were named argosmin a, b and c in order of increasing retention time on a non-polar column.

When geosmin was collected from the exit port of the GC on 0.5 g columns of acid-washed silica which were eluted the next day with cyclohexane, only argosmins a and c were produced. By GC from this mixture argosmin c could be obtained in small amounts. In the original acid treatment of geosmin, hydrochloric acid in methylene chloride (2), mainly argosmins b and c were formed.

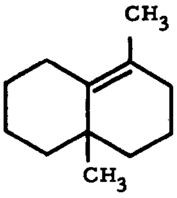
Argosmin c showed two singlet methyl groups in the nmr at 1.05 and 1.62 δ . It (7 mg.) and the mixtures of a + c (31 mg.) and b + c (16 mg.) were degraded using osmium tetroxide then periodate - permanganate (10). The products were separated by column chromatography on silica, tested for acidity on thin-layer plates with indicator spray and treated with 2, 4-dinitrophenylhydrazine (DNP). Argosmin c furnished a neutral oil (diketone) which gave a yellow DNP derivative, mp 205-10°, lacking carbonyl absorbtion in the IR. The mixtures also gave this easily recognizable DNP derivative in addition to acidic materials (keto acids) which yielded poorly or non-crystalline DNP derivatives with carbonyl absorbtion in the IR.

At this point we suspected that argosmin c was 1, 10-dimethyl-1(9)-octalin and were able to verify this by comparison with an authentic sample (11). The two olefins were identical in nmr and IR spectra, GC retention times and the DNP derivatives of their degradation products were also identical. The IR spectrum of geosmin was then sent to Dr. Marshall for comparison with those of the four isomeric 1, 10-dimethyl-9-decalols (12). It matched that of trans-1, 10-dimethyl-trans-9-decalol and we were able to verify their identity by direct comparison. The two samples were identical in nmr spectra, and GC retention times; furthermore the synthetic decalol was transformed to a mixture of olefins identical to the argosmins in GC behavior.

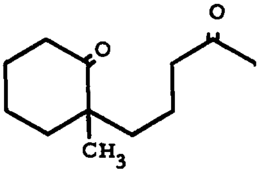
Biogenetically geosmin appears to be a sesquiterpene which has lost an isopropyl group. Geijerene is another example (13).



geosmin



argosmin c



diketone from degradation of argosmin c

Footnotes and References

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14. We wish to thank Dr. J. Berger and the Hoffmann-LaRoche Co. for large scale fermentations for the production of geosmin as well as Drs. Vane and Bommer of the same organization for high resolution mass spectra. We are indebted to Mrs. M. P. Lechevalier for geosmin producing strains of actinomycetes, Mrs. E. M. Fekete for technical assistance, and the U. S. Public Health Service AI 06708 for financial support.