A VOLATILE METABOLITE OF ACTINOMYCETES, 2-METHYLISOBORNEOLO

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During the past five years we have isolated geosmin, trans-1,10-dimethyl-trans-9-deca-

dol from 20 different actinomycetes1*. However, from 4 of these actinomycetes the major volatile component was a crystalline solid with a strong camphor-menthol-like odor. They were Streptomyces lavendulae IMRU 3440-1Y, S. sp. 100-1 (received from Jacob Eren, isolated from a reservoir in Israel), S. sp. AY-219 (received from Benjamin Becker, isolated from soil, Clinton, N. Y.), and Actinomadura sp. 1-15 (received from M. P. Lechevalier, isolated from greenhouse soil). The nuclear magnetic resonance and mass spectra of this solid suggested that it was 2-methylisoborneol (current Chem. Abstr. name: 1,2,7,7-tetra-
methyl-2-norbornanol). The identity was proved by comparison with an authentic sample prepared from camphor and methyl-
magnesium iodide2).

At this point, others reported that 2-
methylisoborneol is the major odorous component of S. antibioticus 5324, S. praecox ATCC 3374 and S. griseus ATCC 101373). Our work confirms this identification and gives additional useful data.

The melting point of 2-methylisoborneol is 170°C (sealed tube), lit. mp. 168°C2). The mass spectrum shows bands in decreasing order of intensity at 107, 95, 41, 93, 43, 79, 55, 91, 94, 135, 108, 150, 77 mass units. The differences from those reported by Medsker, et al. are qualitative, to be expected when comparing mass spectra from different instruments run at different temperatures. More important, the structure of 2-methylisoborneol can be deduced from published generalizations resulting from a comprehensive mass spectral study of norbornane derivatives4). For sample: (A) a strong band at 41 indicates a gem-dimethyl group, (B) weak bands at 57 and 71 mean no gem-dimethyl group in position 3 (as in fenchyl alcohol), (C) a strong band at 95 indicates 2 or 3 (depending upon mono or di-substitution at position 7) methyl groups at positions 1 and 4 thru 7, (D) a strong band at 58 (compared to 44, 72 and 86) means a methyl substituent at position 2 not 3. The four singlet methyl absorption bands in the nmr spectrum show significant differences in line width which are due to long range spin-spin couplings characteristic of this ring system5).

Borneol has been isolated from some fermentations to which α-pinene or cam-
phene had been added6). However, 2-
methylisoborneol was previously unknown in nature. Eleven-carbon terpenoids are rare; the two lactones in Fig. 1 have each been isolated from several plants7) and trans-2,2,6-trimethylcyclohexylacet acid was found in petroleum8). Most natural terpenoids with an unusual number of carbon atoms seem to be derived biosyn-

thetically from a larger, normal (i. e. C10, C15, C20) terpenoid by loss of carbon. Examples are cryptone9), geosmin, cogejerine10), and gibberellic acid. Thus, 2-
methylisoborneol might be biosynthesized as shown in Fig. 2 although, superficially it appears to be a typical monoterpenic unit (borneol) plus a methyl group.

Fig. 1. Some naturally occurring C11 terpenoids: 2-methylisoborneol and two lactones from plant sources.
Fig. 2. Possible biosynthesis of 2-methylisoborneol from a typical sesquiterpene precursor.

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Literature cited