the formula R_2SbBr_8 and $R_3Sb_2Br_{14}$. At or near liquid air temperature, colors ranging from bright orange to red have been obtained. The color change is reversible and changes from black to red to orange as the temperature is lowered.

The preliminary investigations carried out on the $R_xSb_yBr_z$ salts confirm the need for additional extensive study. Further investigations into the color change with temperature and a study of their magnetic properties are planned. The detailed single crystal structure determinations of several of these salts by X-ray diffraction are currently in progress. More complete details concerning the crystal structure of $(NH_4)_4Sb_2Br_{12}$, as well as of those under current investigation, will be reported later.

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A New Acyclic Acid Metabolite in Camphor Oxidation

Sir:

Previous studies[1-3] revealed types of reactions and enzymes which oxygenate and cleave the carbocyclic rings of the bicyclic bornane nucleus. Figure 1 depicts the known intermediates, I → VII,[4,5] in a pathway of

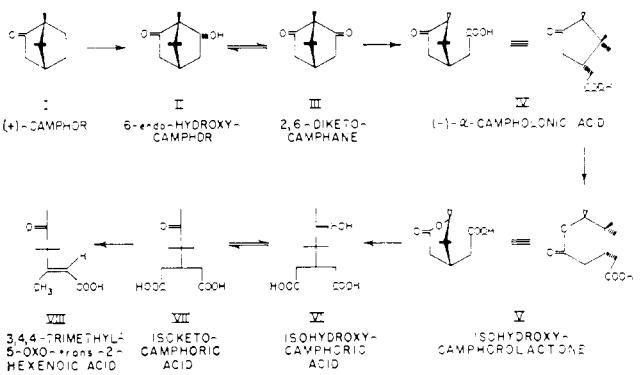

Figure 1. Oxidation pathway of (+)-camphor by bacterial strain T_1. The stereochemistry of the C-10 methyl has not been established rigorously [M. Harispe and D. Mea, *Bull. Soc. Chim. France*, 1340 (1962)]. Its depiction here does not indicate any stereochemical assignment.

(+)-camphor [(+)-2-bornanone] oxidation by a soil diphtheroid, strain T_1.[6]

This paper identifies a branched 9-carbon acid (3,4,4-trimethyl-5-oxo-*trans*-2-hexenoic acid, VIII) isolated from the medium and presumed to arise from the 10-carbon skeleton VII by decarboxylation following α,β-dehydrogenation, possibly as a coenzyme A thioester.[7]

The pathway outlined in Figure 1 was deduced from our identification[3,5] of the intermediates and their use in enzyme studies. The steps include direct 6-*endo*-hydroxylation of camphor to II, its DPN mediated dehydrogenation by an inducible dehydrogenase[2,8] to form 2,6-diketocamphane (III) and hydrolysis to (−)-α-campholonic acid (IV) by a stereospecific β-diketone hydrolase.[3] Cleavage of the second carbocyclic ring adjacent to the ketone, by a keto–lactonase system similar to the pseudomonad pathway,[9] is suggested by the analogous reaction on fenchone[10] and the presence of a specific inducible DPNH-coupled alcohol dehydrogenase,[11] which reduces isoketocamphoric acid (VII) to the hydroxy acid VI.

Experimental details have been described for growth of the organism and for extraction of the culture medium with methylene chloride to give neutral and acidic intermediates.[5] The crude acids were separated into ketonic and nonketonic acid fractions by Girard's reagent T. Separation of the unreacted "non-ketonic" components was effected on 2.1 g. of sample by preparative thin layer chromatography on silica gel plates prepared by the modified spreading techniques of Lees and DeMuria.[12] Separation of at least six distinct bands, as visualized by an ethanolic bromcresol green spray, was achieved by developing with acetic acid–chloroform (10:90 v./v.). The fastest moving band (R_f 0.74) was scraped from 35 chromatographic plates, 20 × 20 cm., and extracted with ether to yield 76 mg. of crystalline VIII, m.p. 123°, neut. equiv. 172 ± 2 (calcd. 170). Gas–liquid chromatography of the methyl ester gave a single peak; thin layer chromatography similarly showed only one component, detectable by ultraviolet absorption, acidic properties to ethanolic bromcresol green spray, and positive reaction with 2,4-dinitrophenylhydrazine reagent.[13]

This acid showed infrared absorption ($CHCl_3$) at 1691 cm.$^{-1}$ (carbonyl) and 1629 cm.$^{-1}$ (conjugated olefin), and an ultraviolet maximum, ϵ 9000 at 210 mμ (EtOH), which corresponds to an α,β-unsaturated acid.[14] The nuclear magnetic resonance spectrum ($CDCl_3$) assigns an olefinic methyl peak at C-3 (τ 7.92, doublet), *cis* to the carboxyl, and an olefinic proton peak at C-2 (τ 4.04, multiplet);[15] it also contains peaks at τ −1.75 (1H, singlet carboxyl proton), τ 7.92 (3H, acetyl singlet, overlapping with the doublet of the allylic methyl), and τ 8.70 (6H, two singlet methyl groups). The groups defined by the ultraviolet and nmr. spectra (CH_3—C=CH—COOH, $(CH_3)_3$ = $C_7H_{14}O_2$) account for 130 mass units. The equivalent weight indicated by titration agrees satisfactorily with the molecular formulas $C_9H_{14}O_3$ (mol. wt. 170) and $C_8H_{14}O_4$ (mol. wt. 174), but only the former can account for the nmr. spectrum

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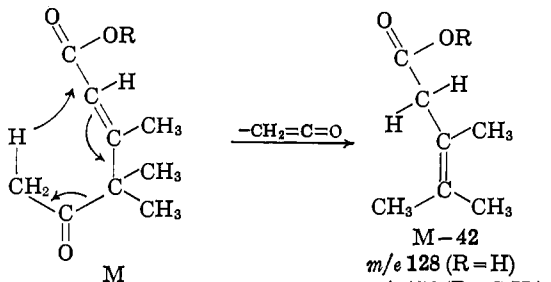
with its two aliphatic methyl groups and second deshielded methyl group. Only one structure is finally allowed: 3,4,4-trimethyl-5-oxo-*trans*-2-hexenoic acid (VIII).

To confirm structure VIII, the acid was synthesized. 3,3-Dimethyl-2,4-pentanedione, b.p. 173° (lit. 173°),[16] giving a single peak on gas–liquid chromatography, was stirred for 24 hr. at room temperature with triethyl phosphonoacetate[17] to give a 71% yield (based on recovered diketone) of ethyl 3,4,4-trimethyl-5-oxo-*trans*-2-hexenoate (IX), b.p. 76–80° (0.4 mm.), λ_{max} 222 mμ, ε 12,600 (*Anal.* Found: C, 66.33; H, 9.00). When this ester was saponified at room temperature with potassium hydroxide in methanol, crystalline compound VIII, m.p. 128–129°, (*Anal.* Found: C, 63.72; H, 8.30) was obtained on acidification. The synthetic acid was identical with the natural acid in ultraviolet, infrared, n.m.r. and mass spectra; a mixture melting point was undepressed.

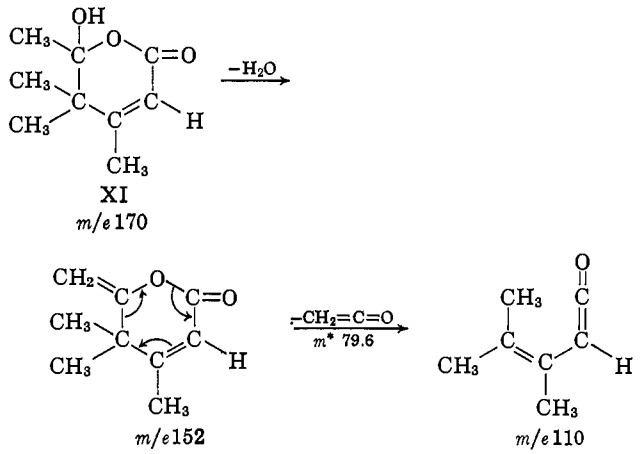
Extraction of the mother liquors with ether yielded two isomers of VIII: 4,4-dimethyl-3-methylene-5-oxohexanoic acid (X), m.p. 53° (*Anal.* Found: C, 63.52; H, 8.26), whose n.m.r. spectrum contained olefinic protons at τ 4.75 and τ 4.70 and a singlet methylene at τ 7.00, but only 1 deshielded methyl, at τ 7.89, together with the two aliphatic methyls at τ 8.75; and a very small amount of the sterically less favorable 3,4,4-trimethyl-5-oxo-*cis*-2-hexenoic acid, existing predominantly as the δ-lactol XI, m.p. 152–154°, λ_{max} 222 mμ (ε 10,400), infrared band at 1710 cm.$^{-1}$, whose n.m.r. spectrum indicates an olefinic proton at τ 4.20, an olefinic methyl's broad singlet at τ 8.04, a lactol methyl singlet at τ 8.41, and a six-proton singlet at τ 8.83.

The mass spectra of the isomeric acids are of interest. That of VIII has its highest mass peak at *m/e* 128 (M − 42), and that of its ethyl ester (IX) shows only a very small molecular ion peak at *m/e* 198, but a very intense peak at *m/e* 156 (M − 42). Apparently, the molecular ions from VIII and IX both lose ketene (42 m.u.) rapidly from C-5 and C-6, suggesting the novel fragmentation shown. The mass spectrum of the isomeric acid XI,



existing predominantly in the δ-lactol form shown, contains neither a molecular ion nor an ion at M − 42. This isomer fragments by initial loss of water, followed by loss of ketene, to give peaks at *m/e* 152 (M − 18) and *m/e* 110 (M − 60), respectively. This sequence is readily explained by the fragmentations shown.

Among the mass spectra of the isomers, only that of X contains a molecular ion peak at *m/e* 170; fragmentation occurs along several pathways, but loss of ketene is minor.



The reactions from IV to VIII have not been documented by study of their enzymatic catalysis by extracts from camphor-grown cells. The suggested conversion of IV to V is analogous to the Baeyer–Villiger oxidation of ketones with peracids,[18] the enzymatically documented biological reactions in steroid[19] and camphor[20] oxidation by microorganisms, and the accumulation of fencholides[10] by the strain T_1 used in these studies. Additional support for the proposed mechanism derives from the presence of an enzyme which catalyzes the rapid oxidation of DPNH in the presence of isoketocamphoric acid (VII).[11] Thus, it may be inferred that isohydroxycamphoric acid (VI) and its lactone (V) are intermediates. The conversion of isoketocamphoric acid (VII) to hexenoic acid VIII is analogous to the sequence mevalonic acid 5-pyrophosphate → dimethylallyl pyrophosphate,[21,22] and to the isoprenoid degradation.[23]

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Valence Isomerization of a *cis*-Dienone to an α-Pyran

Sir:

The valence isomerization between *cis*-dienones and α-pyrans has been invoked in several instances[1] to

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