stant specific radioactivity over three cycles after the initial recrystallization. This evidence clearly indicates that 2,3-oxido-22,23-dihydrosqualene is cyclized enzymically to 24,25-dihydrolanosterol. In addition, it has been found that ^{3}H-labeled 2,3-dihydrosqualene[10] upon aerobic incubation with rat liver homogenate affords a radioactive product which is chromatographically identical with cholesterol.

The enzymic cyclization of **5** occurs at a rate which is comparable to that for 2,3-oxidosqualene (**1**). By comparison, the cyclization of the dioxide **4** is considerably slower.

If it can be assumed that the enzyme responsible for the cyclization of **4** and **5** is that which cyclizes 2,3-oxidosqualene, as seems highly probable, that enzyme does not interact covalently with the Δ^{22} double bond of **1**. Further studies are in progress to determine whether other structurally modified analogs of **1** can be cyclized to sterol systems under the influence of 2,3-oxidosqualene–sterol cyclase. It is noteworthy that 9,10-dihydrosqualene is epoxidized but not cyclized in rat liver homogenate.[2,12,13]

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(13) We are grateful to P. R. Ortiz de Montellano, K. Lin, and P. D. G. Dean for valuable assistance during the course of this study.
(14) Radcliffe Institute Scholar, 1966–1967.

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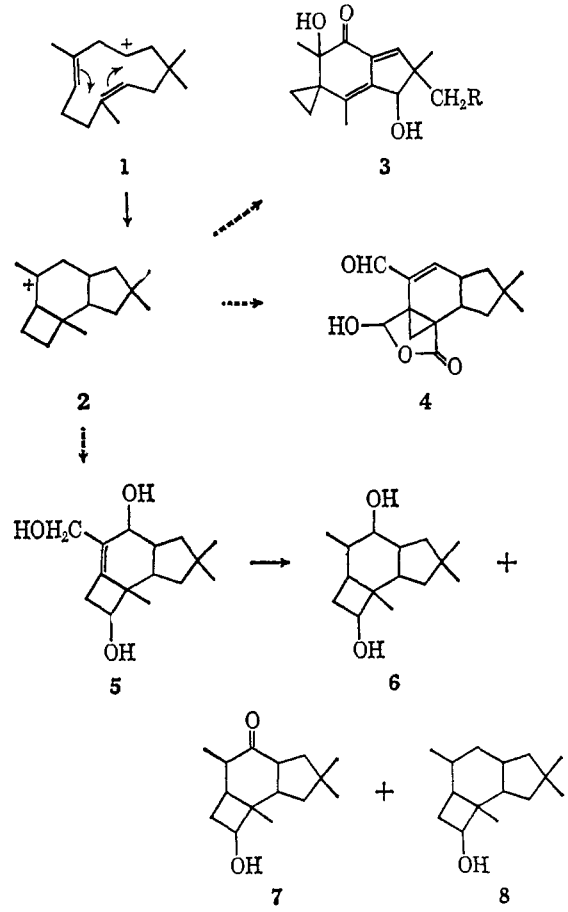

The Structure of Illudol, a Sesquiterpenoid Triol from *Clitocybe illudens*

Sir:

We recently proposed a biogenetic scheme for the formation of the sesquiterpenoids illudin-S (**3**, R = OH) and -M (**3**, R = H). This involved a humulene-type precursor **1** and the tricyclic cation **2**.[1] A similar route has also been proposed for the genesis of marasmic acid (**4**).[2] We have now found that a third metabolite of *Clitocybe illudens*, "illudol" (the "inactive compound" [3]), has structure **5**, with the same carbon skeleton as the postulated precursor (**2**) of the illudins.

Illudol, mp 130–132°, $[\alpha]_D$ −116° (*c* 0.42, 95% ethanol), analyzed for $C_{15}H_{24}O_3$, formed a triacetate, and was monounsaturated (λ_{max} 207 mμ (ϵ 9400)), and hence tricyclic. The mass spectrum did not show the molecular ion peak (mol wt 252) but gave peaks at *m/e* 234 (M − 18) and 216 (M − 2(18)). The nmr spectrum showed signals for three tertiary methyl groups (τ 9.03, 9.0, and 8.92) and a singlet at τ 5.78 (2 H) partly overlapping multiplets due to two other protons. On acetylation, this singlet was shifted to τ 5.45, confirming the presence of a primary hydroxyl group, possibly allylic. Absence of any other low-field signals indicated that the double bond was tetrasubstituted. Signals in the triacetate at τ 5.37 (1 H, triplet) and 4.7 (1 H, poorly resolved doublet) indicated that there were two secondary hydroxyl groups in the parent compound.

Catalytic hydrogenation of **5** with palladium on charcoal gave a complex mixture from which three crystalline compounds were isolated by chromatography on silica gel. One was a diol (**6**), $C_{15}H_{26}O_2$, mp 94–95°. Its nmr spectrum integral showed the presence of four methyl groups (signals at τ 9.09, 8.99, and 8.95), indicating that hydrogenolysis of the primary hydroxyl group had taken place. In agreement, there were now only two protons α to oxygen, *viz.*, at τ 6.6 (broad peak) and 5.47 (triplet), shifted to τ 5.09 and 4.67, respectively, on addition of CCl_3CONCO. The second product was a keto alcohol (**7**), mp 110–112° (mol wt 236), ν_{max} 3290 and 1709 cm^{-1}. The formation of this compound by hydrogenolysis of the primary hydroxyl group and migration of the double bond in **5** indicated that one of the secondary hydroxyl groups in **5** was allylic and present in a six-membered ring. The third product of hydrogenation, mp 87–91°, ν_{max} 3280 cm^{-1}, was the monoalcohol **8**.

Treatment of illudol with palladium on charcoal at 280° gave a mixture of hydrocarbons. The major component, isolated by vapor phase chromatography, was identical with 2,2,4,5,6-pentamethylindan[2] (ultraviolet, infrared, nmr). Formation of a C_{14} bicyclic aromatic compound from illudol on dehydrogenation, considered in conjunction with the above evidence, suggested that the third ring of this tricyclic triol was four membered. In confirmation, oxidation of **6** and **7** with Jones reagent[4] gave a diketone, ν_{max} 1782 (cyclobuta-

(1) T. C. McMorris and M. Anchel, *J. Am. Chem. Soc.*, 87, 1594 (1965).
(2) J. J. Dugan, P. de Mayo, M. Nisbet, J. R. Robinson, and M. Anchel, *ibid.*, 88, 2838 (1966).
(3) M. Anchel, A. Hervey, and W. J. Robbins, *Proc. Natl. Acad. Sci. U. S.*, 36, 300 (1950).
(4) A. Bowers, T. G. Halsall, E. R. H. Jones, and A. J. Lemin, *J. Chem. Soc.*, 2548 (1953).

none) and 1715 cm^{-1} (cyclohexanone); this characteristic cyclobutanone absorption was observed also in the infrared spectrum of the monoketone (ν_{max} 1783 cm^{-1}) from the alcohol **8**.

The mass spectra of **6** and **7** showed intense peaks at *m/e* 194 (M − 44, 84% of base peak) and 192 (M − 44, base peak), respectively. These were probably formed by cleavage of the cyclobutanol ring with loss of CH_2CHOH.[5]

The presence of an allylic secondary hydroxyl in the six-membered ring, a tetrasubstituted double bond carrying a hydroxymethyl (and no methyl group), and a cyclobutane ring fixed the carbon skeleton of illudol. The position of the hydroxyl in the cyclobutane ring was indicated by the splitting pattern of the proton α to it (in the nmr spectra of **6** and **7**), leading to the unique structure **5** for illudol.

In accordance with its terpenoid nature, illudol incorporated radioactivity from [2-C^{14}]mevalonic acid.

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(5) *Cf.* cyclobutanol: H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds," Holden-Day, Inc., San Francisco, Calif., 1964, p 42.

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The Isolation and Characterization of Two Diastereomeric Ammonium Salts Differing Only in Nitrogen Configurations

Sir:

The inversion of nitrogen of a tertiary amine is sufficiently rapid to prevent detection of the two diastereomeric forms in the proton magnetic resonance spectrum of a compound such as tropane.[1] Measurement of the spectrum in acidic medium permits observation of two signals for the nitrogen substituent due to a decrease in the rate of inversion on protonation of the nitrogen.[1,2] The reversibility of the protonation has prevented isolation of the two isomeric ammonium salts, however. We wish to report the isolation of two diastereomeric ammonium salts which differ only in the configuration of the ammonium nitrogen. This represents the first example of such isomers which are stable in solution at room temperature.

Dehydration of 3-phenyltropine (**1**) in 40% hydrobromic acid formed α-3-phenyltropidine hydrobromide (**2a**),[3] mp 179.5–181.0°, λ_{max}^{EtOH} (log ϵ) 216.2 (4.01), 247.9 (4.11), and 290.3 mμ (2.39). The base, 3-phenyltropidine (**3**), was prepared and converted to the known hydrochloride[4] and methiodide[5] whose properties were identical with those reported. Reaction of the base **3** with hydrogen bromide in anhydrous ether caused the precipitation of β-3-phenyltropidine (**2b**), mp 180–182°, λ_{max}^{EtOH} (log ϵ) 216.2 (4.07), 247.1 (4.17), and 290.0 mμ (2.40). The nonidentity of the α and β forms of 3-phenyltropidine hydrobromide (**2**) was clearly evident from the proton magnetic resonance (Figure 1) and infrared spectra and the X-ray powder pattern,[6] although the ultraviolet and mass spectra of **2a** and **2b** were nearly identical.

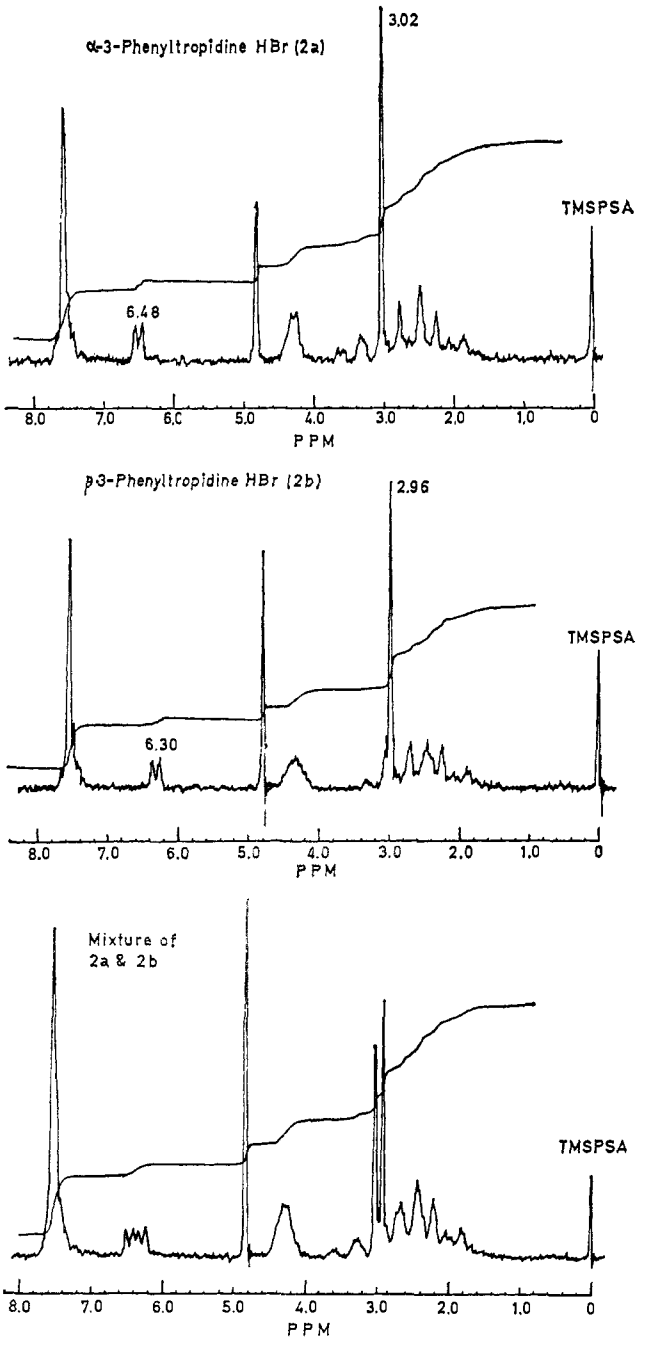

Figure 1. The proton magnetic resonance spectra of α-3-phenyltropidine hydrobromide (**2a**), β-3-phenyltropidine hydrobromide (**2b**), and a mixture of the two isomers formed on heating a solution of either. The spectra were determined in deuterium oxide using the sodium salt of trimethylsilylpropanesulfonic acid (TMSPSA) as the internal standard.

(1) (a) J. C. N. Ma and E. W. Warnoff, *Can. J. Chem.*, 43, 1849 (1965); (b) G. L. Closs, *J. Am. Chem. Soc.*, 81, 5465 (1959); (c) D. L. Griffith and J. D. Roberts, *ibid.*, 87, 4089 (1965).

(2) R. W. Horobin, J. McKenna, and J. M. McKenna, *Tetrahedron Suppl.*, 7, 35 (1966).

(3) All new compounds gave correct elemental analyses and infrared, ultraviolet, and nmr spectral data consistent with the assigned structures.

(4) M. R. Bell and S. Archer, *J. Am. Chem. Soc.*, 82, 4638 (1960).

(5) A. C. Cope and D. A. D'Addieco, *ibid.*, 73, 3419 (1951).

(6) The authors wish to thank Professor Helmut M. Haendler for assistance in obtaining and interpreting these data.