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# 1-VINYLMENTH-4(8)-ENE, A TERPENOID HYDROCARBON FROM *MENTHA CITRATA*

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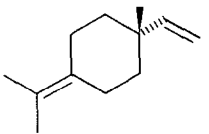
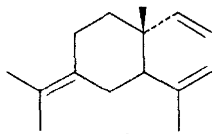
**Key Word Index**—*Mentha citrata*; Labiatae, $C_{12}$ terpenoid; 1-vinylmenth-4(8)-ene.

*Mentha citrata* has been studied in the past for its essential oil and the early reports deal with the isolation of the oil and determination of its physico-chemical characteristics [1, 2]. No attempt has been made so far to fractionate or separate the constituents of the oil. The present work describes the isolation of a new steam-volatile terpenoid compound.

The essential oil (5 g, 1.3%) obtained on steam distillation of the fresh herb of *M. citrata* (380 g) was repeatedly chromatographed on a Si gel column using (i) petrol (40–60°), (ii) petrol (60–80°) and (iii) petrol (60–80°)–benzene (1:1) as eluent. Besides the known constituents, solvent (iii) afforded a new terpenoid hydrocarbon (35 mg) which was further purified by $AgNO_3$ impregnated Si gel-G preparative TLC (*n*-hexane–benzene, 1:3). Compound **1** (25 mg, 0.0006%) was found to be homogeneous in GLC (SE-30, temp. 160°). The terpenoid **1**, $C_{12}H_{20}$ ($M^+$ at *m/e* 164) (Found: C, 87.81; H, 12.18; $C_{12}H_{20}$ requires: C, 87.80; H, 12.20%) was found to have a novel structure based on the following spectral data: IR, 1220 (quart $-\overset{|}{\underset{|}{C}}-$) and 915 $cm^{-1}$ ($-C{=}CH_2$). $^1H$ NMR: $\delta$ 1.11 (3 H, *s*, tert. $-CH_3$) 1.50, 1.55 (each 3 H, *s*, $=C\langle{CH_3 \atop CH_3}$), 1.0–1.5 (4 H, *m*, $-CH_2$), 1.6–2.1 (4 H, *m*, allylic-$CH_2$) and signals for an ABX-type system, i.e. a doublet of doublets at 5.75 (1 H, $J_{AX} = 17$, $J_{BX} = 11$ Hz) as well as two doublet of doublets at 5.1 (1 H, $J_{AX} = 17$, $J_{AB} = 2$ Hz) and at 4.9 (1 H, $J_{BX} = 10$, $J_{AB} = 2$ Hz).

The MS fragmentation pattern of **1** showed prominent peaks at *m/e* 164 ($M^+$), 149 ($M^+ - CH_3$, base peak, **a**), 136 ($M^+ - C_2H_4$), 121 ($M^+ - C_3H_7$) and a peak at 93 (corresponding to ion **b**) in agreement with the assigned structure. Furthermore, the downfield shift of the methyl group at C-1 ($\delta$ 1.11) in the $^1H$ NMR spectrum of **1** suggested [3, 4] it to be axially oriented which is also supported by the fact that the loss of the axial methyl group relieves the strain to give a stable ion and consequently affords the base peak at *m/e* 149 in the MS.


**1**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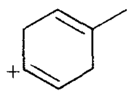
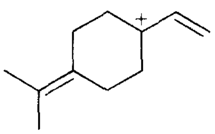

**b**


**a**

On the basis of the above physical data, the structure 1-vinylmenth-4(8)-ene (**1**) has been proposed.

Previously no $C_{12}$ terpenoid was known to occur in nature and 1-vinylmenth-4(8)-ene is now the first example. It is probable that **1** is biosynthesized by the elimination of the isopropenyl group from an elemene-type sesquiterpene (**2**) by an obscure mechanism.

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