

CHEMICAL INVESTIGATION OF THE ESSENTIAL OIL OF *LAGGERA AURITA*

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ABSTRACT

The essential oil of *Laggera aurita* on extensive application of chromatographic technique afforded C_{27} (I), C_{32} (II) alkanes, together with δ -cadinene, 2, 3-dimethoxy-*p*-cymene (a new aromatic ether), laggerol (a new sesquiterpenic secondary alcohol), α -cadinol and *m*-menth-6-en-8-ol. The identities of these compounds have been ascertained on the basis of their physical, chemical and spectral data.

THE plant *Laggera aurita*¹ is an annual shrub growing throughout Madhya Pradesh. In Malwa region it is known as 'Kukronda'. It flowers during December to February and bears pink coloured flowers. A survey of literature shows that no work has been done on the chemical examination of the steam volatile constituents of the plant. In the present work, the whole plant at full flowering stage was subjected to steam distillation which gave a dark yellow oil (0.04%) with a characteristic sweet smell. The oil shows the presence of nine components on TLC as well as on GLC examination, seven of them have been identified as shown in the abstract.

EXPERIMENTAL

The essential oil was found to have the following physical and chemical constants: n_D^{26} , 1.498; d_4^{26} , 1.0742; $(\alpha)_D^{26}$, ± 0 ; acid value, 0.76; ester value, 5.23 and boiling range, 54–114°/1 mm.

The oil was separated into acidic and neutral parts by washing with sodium hydroxide solution (5%). No work was possible on the acidic portion due to paucity of the material. The neutral portion (10 g) was chromatographed over neutral alumina grade II (1 : 30) and three major fractions were collected by eluting the column with petroleum ether, benzene and ether.

Petroleum ether fraction (3.5 g) was again chromatographed over active silica-gel followed by silica-gel impregnated with silver nitrate (15%) which gave three compounds A, B, and C in TLC pure form.

Compound 'A', b.p. 170–172°/13 mm; n_D^{21} , 1.432 analysed for $C_{27}H_{56}$. This was crystallised from chloroform-methanol as colourless plates (0.24 g), m.p. 60–61°. ν_{max} , 2900, 1460, 1350, 1020, 840, 732 and 722 cm^{-1} and the NMR signals at 8.70 and 8.20 τ . The compound 'A' was characterised as *n*-heptacosane^{2,3} by comparison of its IR and NMR spectra with that of an authentic sample.

Compound 'B' b.p. 240°/13 mm. n_D^{27} , 1.442 analysed for $C_{32}H_{60}$. This was crystallised from chloroform-methanol as colourless plates (0.13 g), m.p. 71–72°. ν_{max} , 2950, 1470, 1385, 1038, and

722 cm^{-1} and NMR signals at 8.70 and 8.20 τ . It was characterised as *n*-dotriacontane^{4,5} by comparison of its IR and NMR spectra with that of an authentic sample.

Compound 'C', b.p. 125–127°/2 mm; n_D^{29} , 1.502 analysed for $C_{15}H_{24}$. ν_{max} , 837 (trisubstituted double bond), 1385 and 1370 (isopropyl group), and 2940 and 1450 cm^{-1} (C–H and C–CH₃). The IR spectrum of this compound is superimposable with that of δ -cadinene^{6,7}. The identity was confirmed through catalytic dehydrogenation, selenium dehydrogenation and ozonolysis.

Benzene fraction (2.3 g) was chromatographed over silica-gel impregnated with silver nitrate (15%), which gave two compounds 'D' and 'E' in TLC pure form.

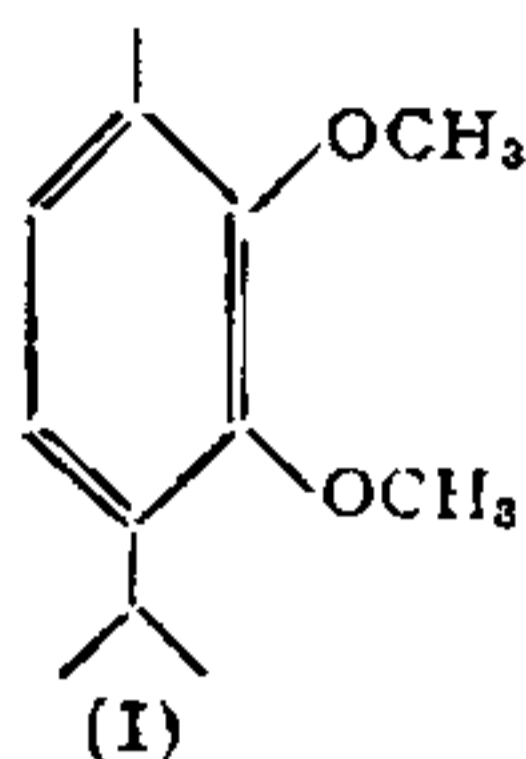
Compound 'D' was distilled under reduced pressure, b.p. 97–98°/0.5 mm; n_D^{29} , 1.486; $(\alpha)_D^{29}$, ± 0 analysed for $C_{12}H_{18}O_2$ with 2 (OCH₃)⁺ groups (M, m/e : 154). ν_{max} , 2986 (C–H), 1379, 1362 and 1178 (isopropyl group), 1210, 1157 and 1065 (phenolic ether), 850 (two free adjacent hydrogen atoms in the aromatic ring) and 805 cm^{-1} (1 : 2 : 3 : 4 tetra substituted benzene)⁸. NMR (CCl₄, τ), 8.88 and 8.76 (6 H, two methyls of isopropyl groups), 7.80 (3 H of one methyl group); 3.30 and 3.26 (2 H, aromatic); 6.18 (6 H of two methoxyl groups) and 6.90–6.40 (*m*, of one benzylic proton). On comparing the NMR spectrum with that of *p*-cymene, there was an agreement in all the signals except 6.18 τ (two methoxyl groups). This shows that compound 'D' has *p*-cymene skeleton with two methoxyl groups.

The λ_{max} (log ϵ) of 'D' 228 $m\mu$ (3.91), 285 $m\mu$ (3.62) and the ratio of wavelength of the secondary to primary bands is fairly close to 1.22, which agrees with the presence of substituted benzene having –OCH₃ group.

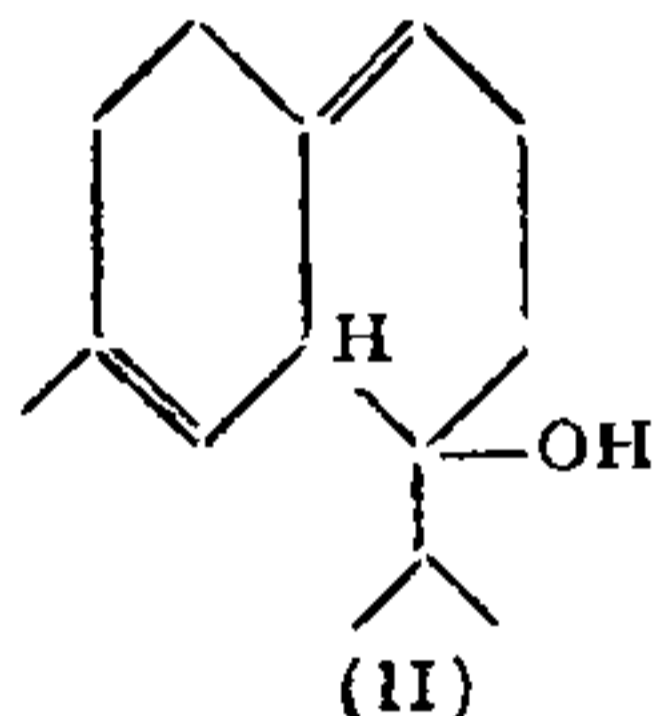
In the light of the aforesaid evidence, a tentative structure (I) has been proposed for this new ether and named as 2,3-dimethoxy-*p*-cymene.

Uptill now only 2,5-dimethoxy-*p*-cymene and 2,5-dihydroxy-*p*-cymene^{9,10} have been reported to occur in several essential oils but 2,3-dimethoxy-

p-cymene has not yet been reported. However, it occurs in the essential oil of *Blumea membranacea* as presently reported by Joshi¹¹.



Compound 'E', b.p. 109°/3.5 mm; n_D^{20} , 1.586; $(\alpha)_D^{20}$, -12.07° analysed for $C_{15}H_{20}O$ (M^+ , m/e; 222). ν_{max} , 3430 (hydroxyl group), 1365, 1378, 1165 (isopropyl group), 890, 865 and 800 (trisubstituted double bond) and 2900 cm^{-1} (C-H). NMR (CCl_4 , τ): 9.18, 9.12, 9.08 and 9.02 (2d, 6H, 2 CH_3 of isopropyl group); 8.38 (s, 6H, two methyl groups on two double bonds); 8.09 (broad s, three methylene groups conjugated to the double bonds); 4.79 (s, a proton on the trisubstituted double bond) and 7.72 (broad s, disappeared on D_2O exchange, hydroxyl group). The compound, therefore, seems to be a sesquiterpenic alcohol.



On selenium dehydrogenation in the presence of nitrogen, this compound gave cadalene in considerable yield which has been identified on the basis of melting point of its picrate. The formation of cadalene showed the presence of bisabolene skeleton in this compound. Therefore, the following tentative structure (II) has been proposed for it and named as Lagerol.

Ether fraction (3.12 g) of neutral oil was chromatographed over silica-gel impregnated with silver nitrate (15%) which gave two compounds 'F' and 'G' in TLC pure form.

Compound 'F', b.p. 163–165°/3 mm; m.p. 70–71°; n_D^{20} , 1.4942; $(\alpha)_D^{20}$, -20.06° analysed for $C_{15}H_{26}O$ and was identified as α -cadinol¹² by IR, NMR and chemical evidence.

Compound 'G', b.p. 148°/8 mm; n_D^{20} , 1.471; $(\alpha)_D^{20}$, 29.40° analysed for $C_{10}H_{18}O$ and was identified as *m*-menth-6-en-8-ol¹³ by IR, NMR and chemical evidence.

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STUDIES ON QUINAZOLONES DERIVATIVES

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THE discovery of various types of quinazolones as antimalarials¹, CNS potent² and antibacterials³ as well as their hydrazides as anti-inflammatory agents⁴

have created the interest of authors to prepare some 6-bromo-2-(β -diethylaminoethylthio)-3-aryl (or alkyl)-4 (3H) quinazolones and 6-bromo-2-carboethoxymethylthio-3-aryl-4 (3H) quinazolones as chemotherapeutical interest. The syntheses were carried out by the reaction of 6-bromo-3-aryl (or alkyl)-2-thio-4 (3H) quinazolones with equivalent

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