SESQUITERPENES FROM LANSIUM ANAMALAYANUM*

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Key Word Index—Lansium anamalayanum; Meliaceae; a-gurjunene; a-bergamotene; β-bisabolene; 'chigadmarene'.

Abstract—The essential oil from the wood of Lansium anamalayanum Bedd. is shown to consist essentially of (−)-a-gurjunene (34%), (−)-a-trans-bergamotene (26%) and (−)-β-bisabolene (35%). The previously reported 'chigadmarene' has been found to be impure a-gurjunene. This essential oil is the richest known source for (−)-a-trans-bergamotene.

The essential oil from the wood of Lansium anamalayanum Bedd. (Kannada: Chigadmeri) has been the subject of several studies and the presence of bisabolene and a new sesquiterpene, chigadmarene, has been reported. Based on degradative studies, chigadmarene was tentatively assigned structure I. On securing a sample of chigadmarene, isolated by earlier workers, it was found by GLC to be a mixture of four components, with one of these accounting for about 75%. This necessitated a re-examination of the whole problem and we report the results in the present communication.

A fresh sample of the essential oil, as obtained by steam distillation of the trunk wood of Lansium anamalayanum was found to have physical characteristics quite close to those reported by the earlier investigators. From its IR spectrum and b.p. range, it was obvious that the essential oil is chiefly, if not entirely, a mixture of sesquiterpene hydrocarbons. GLC of the material showed it to consist of at least six components with relative retention times (RR,) of 1.00 (33.5%), 1.18 (25.5%), 1.42 (1%), 1.66 (3%), 2.00 (35%) and 2.33 (2%). By a combination of fractional distillation and preparative GLC, the three major components (RR,: 1.00, 1.18 and 2.00) could be obtained pure by GLC and TLC (AgNO₃-silica gel) and have been identified (physical constants, spectral data) as (−)-a-gurjunene (II), (−)-a-trans-bergamotene (III) and (−)-β-bisabolene (IV). Sesquiterpene III has so far been


1 JOIS, H. S., MANJUNATH, B. L. and RAMALAH, D. V. (1941) J. Mysore Univ. 8, 171.
2 SASTRY, S. G. (1973) Quart. J. Mysore Forest Assoc. 5, in press.
found in five different essential oils, but only as a trace component. The essential oil from *Lansium anamalayanum* is thus, by far the richest known source for this compound. The so-called new sesquiterpene 'chigadmarene' was recognized by GLC to be essentially (about 75%) α-gurjunene contaminated with α-bergamotene, β-bisabolene and an hitherto unrecognized component (RR, = 1.42). The diketone obtained earlier by ozonolysis of 'chigadmarene', appears to be identical (m.p. of semicarbazone, elemental analysis) with the diketone prepared by Treibs and Merkel by KMnO₄ oxidation of α-gurjunene.

At the time the present investigations were being carried out, the structure of bergamotene (III) rested essentially on its IR and PMR spectra. Hence, attempts were made to correlate this product with Bhattacharyya's β-bergamotene (from Indian valerian root oil) which was considered as a result of synthesis of β-cis-bergamotene (V) to be the trans-isomer (VI).

In view of the known similar behavior of α- and β-pinences on catalytic hydrogenation, it was anticipated that the products from the α- and β-bergamotenes would be essentially identical. An authentic sample of the tetrahydro derivative of Bhattacharyya's β-bergamotene was therefore prepared by its hydrogenation over PtO₂–AcOH. However, this product proved to be completely different (IR, NMR) from the tetrahydro-derivative obtained under the same conditions from our α-bergamotene. Similarly, exposure of Bhattacharyya's β-bergamotene to N-lithioethylenediamine failed to give any product corresponding to α-bergamotene (III). Since, the structure of α-trans-bergamotene has been recently confirmed by a total synthesis, the structure of the so-called 'β-bergamotene' from Indian Valerian root calls for a reinvestigation, and this is also obvious from the fact that synthetic β-trans-bergamotene has been found to be different from Bhattacharyya's β-bergamotene.

**EXPERIMENTAL**

All b.ps are uncorrected. Optical rotations were measured at room temp. (27 ± 2°) in CHCl₃. IR spectra were recorded as smears on a Perkin–Elmer Infracord model 137E. PMR spectra were taken in 10–20% soln. in CCl₄ with TMS as internal standard, on a Varian A60 spectrometer; signals are recorded in δ (ppm)

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relative to TMS as zero. MS were measured on CEC model 21-110B, using an ionizing voltage of 70 eV and a direct inlet system. TLC was carried out on 15% AgNO₃ silica gel layers (0.3 mm) containing 15% gypsum. Spots were detected with 1% vanillin in 30% aq. H₃PO₄ spray, followed by heating at 100° for 10 min. For analytical GLC a 3 m × 0.6 cm column packed with 20% diethylene glycol polysuccinate on Chromosorb W (60–80 mesh) was used with H₂ as carrier gas; for preparative GLC, the 3 m × 1 cm column was packed with 30% diethylene glycol polysuccinate on Chromosorb W (60–80 mesh).

**Essential oil.** Trunk wood and stout branches of a *Chigadmare* tree growing in the vicinity of Bangalore (Mysore State) were collected and steam-distilled to give a brownish yellow oil (yield 2.1%), which was totally redistilled under vacuum: b.p. 110–118°/9 mm, d₃₀ 0.8961, n₂₀ 1.49, [α]D -94°. GLC was carried out at 160° with gas flow of 30 ml/min. On TLC (AgNO₃-silica gel; solvent: 10% benzene in hexane) the essential oil indicated at least six components having Rf values: 0.09, 0.21, 0.40, 0.77, 0.83 and 0.92.

**Fractionation of essential oil and isolation of major components.** The above essential oil (40.6 g) was fractionated through a spinning band column (Model NF 115, Nestler & Faust, Newark, U.S.A.; theoretical plates: 23) at a reflux ratio of 1:20. The various fractions were monitored by GLC and finally like fractions were pooled to give three major cuts (Table 1). These cuts were next subjected to preparative GLC (temp. 180°; 90 ml H₂/min) to give the major components in 100% purity (GLC, TLC).

<table>
<thead>
<tr>
<th>Cut No.</th>
<th>b.p.</th>
<th>[α]D</th>
<th>Wt (g)</th>
<th>Major component having Rf</th>
<th>Rf</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>105–106°/8 mm</td>
<td>-143°</td>
<td>13.2</td>
<td>1.00</td>
<td>0.92</td>
</tr>
<tr>
<td>2</td>
<td>107–109°/8 mm</td>
<td>-101°</td>
<td>7.8</td>
<td>1.18</td>
<td>0.83</td>
</tr>
<tr>
<td>3</td>
<td>105–107°/4 mm</td>
<td>-48°</td>
<td>18.3</td>
<td>2.00</td>
<td>0.21</td>
</tr>
</tbody>
</table>

(-)-α-Gurjunene (II). The major component from cut No. 1 was redistilled: b.p. 110°/7 mm, n₂₀ 1.4960, d₃₀ 0.9126, [α]D -210°. IR: l₁₁₉₃, 1₁₄₅, 1₁₂₀, 1₁₀₅₅, 9₃₀ cm⁻¹ (strong bands). PMR: two tert. Me (3H, s, 0.81, 1.08 ppm), C=C-H (3H, d, 0.86 ppm, J 7 Hz), C=CH₂ (3H, t, 1.65 ppm, J 0.5 Hz). The compound was identified as (-)-α-gurjunene (II) by comparison with physical constants and spectral data reported in literature.

(-)-α-Trans-bergamotene (III). The chief constituent of cut No. 2 was redistilled to give a colorless oil: b.p. 111°/7 mm, n₂₀ 1.4870, d₃₀ 0.8860, [α]D -51°. IR: 1₁₂₀, 1₁₀₁₀, 8₉₀, 8₃₀, 7₉₀ cm⁻¹ (strong bands). PMR: tert. Me (3H, s, 0.83 ppm), three vinylic Me (total 9H, s, 1.63, 1.68 and 1.70 ppm), two vinylic protons (unresolved 2H m centred at 5.20 ppm). MS: important ions at m/e 204 (M+, 23%), 93 (100%), 119 (86%), 91 (38%), 107 (34%), 105 (33%) and 69 (28%). (Lit.: IR, PMR).

(-)-β-Bisabolene (IV). This was isolated by preparative GLC from cut No. 3 and after redistillation had: b.p. 115–116°/4 mm, n₂₀ 1.4892, d₃₀ 0.8762, [α]D -57°. IR: 1₁₆₄₀, 1₁₁₅₅, 1₁₁₄₅, 1₁₀₵, 1₁₀₁₅, 9₁₅, 9₈₀, 8₃₀ cm⁻¹ (strong bands). PMR: three vinylic Me (total 9H, s, 1.62, 1.66 ppm), -C=CH₂ (2H, s; 4.75 ppm), two -C=CH₂ (1H, m, 5.15 ppm; 1H, m, 5.40 ppm). (Lit.: IR, PMR).

Catalytic hydrogenation of α-bergamotene. (-)-α-Trans-bergamotene (60 mg) in AcOH (5 ml) consumed, at room temp. (32°) and pressure (710 mm), 2 M equivalent of H₂ over pre-reduced PtO₂ catalyst, during 2.5 hr, when further absorption of H₂ ceased. Usual work up gave a product (55 mg): b.p. 130–135° (bath)/5 mm, n₂₀ 1.4672; tetraniromethane test, -ve; GLC, single peak. IR (0.05 mm cell): 1₁₁₅, 1₁₄₅, 1₁₂₀, 1₁₀₅₅, 9₃₀ cm⁻¹ (weak spectrum). (Found: C, 86.57; H, 13.43. C₅H₈ requires: C, 86.46; H, 13.54%). A sample of the tetrahydro derivative prepared from the so-called 'α-bergamotene' from Indian valerian root oil, by catalytic hydrogenation, as described above for α-bergamotene had: b.p. 120–128° (bath)/5 mm, n₂₀ 1.4672, 1₁₁₂₀, 1₁₁₁₀, 1₁₀₸₂, 1₁₀₇₀, 1₉₆₀, 9₃₄, 8₂₂ cm⁻¹. This compound was isolated from a sample of Indian valerian root oil, placed at our disposal by the kind courtesy of Dr. K. K. Chakravarti. The isolation was carried out by chromatography of the oil over AgNO₃-silica gel and the product showed spectral characteristics (IR, PMR) identical to those reported in Ref. 14.