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SESQUITERPENES FROM *LANSIUM ANAMALAYANUM**

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

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

THE ESSENTIAL oil from the wood of *Lansium anamalayanum* Bedd. (Kannada: *Chigadmeri*) has been the subject of several studies[1–4] and the presence of bisabolene and a new sesquiterpene, chigadmarene, has been reported.[3,4] Based on degradative studies, chigadmarene was tentatively[4] 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.[2,3] 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_t) 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_t: 1·00, 1·18 and 2·00) could be obtained pure by GLC and TLC ($AgNO_3$–silica gel[5]) and have been identified (physical constants, spectral data) as (—)-α-gurjunene (II),[6] (—)-α-*trans*-bergamotene (III)[7,8] and (—)-β-bisabolene (IV)[7,9,10]. Sesquiterpene III has so far been

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* Part XLVIII in the series "studies in sesquiterpens". For Part XLVII see PANDE, B. S., KRISHNAPPA, S., BISARYA, S. C. and DEV, SUKH (1971) *Tetrahedron* **27**, 841. Communication No. 1657, National Chemical Laboratory, Poona, India. Abstracted from the Ph.D thesis (Poona University, 1968) of S. Krishnappa.

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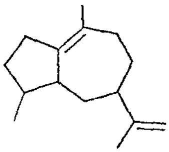
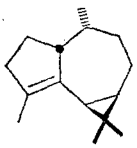
found in five different essential oils,[11] but only as a trace component. The essential oil from *Lansium anamalayanum* is thus, by far the richest known source for this compound. The so-called new sesquiterpene 'chigadmarene' was recognized by GLC to be essentially (about 75%) α-gurjunene contaminated with α-bergamotene, β-bisabolene and an hitherto unrecognized component ($\mathrm{R}R_t = 1{\cdot}42$). The diketone obtained earlier[4] by ozonolysis of 'chigadmarene', appears to be identical (m.p. of semicarbazone, elemental analysis) with the diketone prepared by Treibs and Merkel[12] by $KMnO_4$ oxidation of α-gurjunene.


(I)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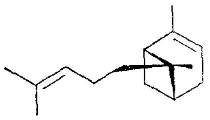
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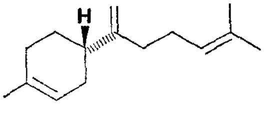
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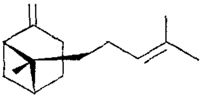
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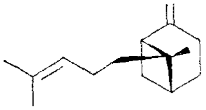
(VI)

At the time the present investigations were being carried out, the structure of bergamotene (III) rested essentially on its IR[13] and PMR[8] spectra. Hence, attempts were made to correlate this product with Bhattacharyya's β-bergamotene[14] (from Indian valerian root oil) which was considered as a result of synthesis[15] of β-*cis*-bergamotene (V) to be the *trans*-isomer (VI).

In view of the known[16] similar behavior of α- and β-pinenes 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 PtO_2–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,[11] the structure of the so-called 'β-bergamotene' from Indian Valerian root calls for a reinvestigation, and this is also abvious from the fact that synthetic β-*trans*-bergamotene has been found to be different from Bhattacharyya's β-bergamotene[11].

EXPERIMENTAL

All b.ps are uncorredted. Optical rotations were measured at room temp. (27 ± 2°) in $CHCl_3$. IR spectra were recorded as smears on a Perkin–Elmer Infracord model 137E. PMR spectra were taken in 10–20% soln. in CCl_4 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% $AgNO_3$ silica gel layers (0·3 mm) containing 15% gypsum.[5] Spots were detected with 1% vanillin in 30% aq. H_3PO_4 spray, followed by heating at 100° for 10 min. For analytical GLC a 3 m × 0·6 cm column packed with 20% diethyleneglycol polysuccinate on Chromosorb W (60–80 mesh) was used with H_2 as carrier gas; for preparative GLC, the 3 m × 1 cm column was packed with 30% diethyleneglycol 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, d^{30} 0·8961, n_D^{30} 1·49, $[\alpha]_D$ −94°. GLC was carried out at 160° with gas flow of 30 ml/min. On TLC ($AgNO_3$-silica gel; solvent: 10% benzene in hexane) the essential oil indicated at least six components having R_f (25°): 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 H_2/min) to give the major components in 100% purity (GLC, TLC).

TABLE 1. FRACTIONATION OF ESSENTIAL OIL FROM *Lansium anamalayanum*

Cut No.	b.p.	$[\alpha]_D$	Wt (g)	Major component having RR_t	R_f
1	105–106°/8 mm	−143°	13·2	1·00	0·92
2	107–109°/8 mm	−101°	7·8	1·18	0·83
3	105–107°/4 mm	−48°	18·3	2·00	0·21

(−)-α-*Gurjunene* (II). The major component from cut No. 1 was redistilled: b.p. 110°/7 mm, n_D^{30} 1·4960, d^{30} 0·9126, $[\alpha]_D$ −210°. IR: 1193, 1145, 1120, 1055, 930 cm^{-1} (strong bands). PMR: two *tert*. Me (3H *s*, 0·81, 1·08 ppm), $C\underline{H}_3$–C–H (3H, *d*, 0·86 ppm, *J* 7 Hz), $C\underline{H}_3$–C=C (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.[6]

(−)-α-*Trans-bergamotene* (III). The chief constituent of cut No. 2 was redistilled to give a colorless oil: b.p. 111°/7 mm, n_D^{30} 1·4870, d^{30} 0·8860, $[\alpha]_D$ −51°. IR: 1120, 1010, 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[13], PMR[8]).

(−)-β-*Bisabolene* (IV). This was isolated by preparative GLC from cut No. 3 and after redistillation had: b.p. 115–116°/4 mm, n_D^{30} 1·4892, d^{30} 0·8762, $[\alpha]_D$ −57°. IR: 1640, 1155, 1145, 1105, 1015, 915, 890, 830, 800 cm^{-1} (strong bands). PMR: three vinylic Me (total 9H, *s*, 1·62, 1·66 ppm), –C=C$\underline{H}_2$ (2H, *s* 4·75 ppm), two –C=C$\underline{H}$–CH_2 (1H, *m*, 5·15 ppm; 1H, *m*, 5·40 ppm). (Lit.: IR,[17] PMR[17]).

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 H_2 over pre-reduced PtO_2 catalyst, during 2·5 hr, when further absorption of H_2 ceased. Usual work up gave a product (55 mg): b.p. 130–135° (bath)/5 mm, n_D^{30} 1·4672; tetranitromethane test, −ve; GLC, single peak. IR (0·05 mm cell): 1185, 1135, 1035, 995, 965, 927, 875 cm^{-1} (weak spectrum). (Found: C, 86·57; H, 13·43. $C_{15}H_{28}$ requires: C, 86·46; H, 13·54%.) A sample of the tetrahydro derivative prepared from the so-called 'β-bergamotene' from Indian valerian root oil, by catalytic hydrogenation, as described above for α-bergamotene had: b.p. 120–128° (bath)/5 mm, n_D^{30} 1·4672. IR spectrum (0·05 mm cell): 1266, 1175, 1100, 1082, 1070, 1028, 960, 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 $AgNO_3$–silica gel and the product showed spectral characteristics (IR, PMR) identical to those reported in Ref. 14.

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