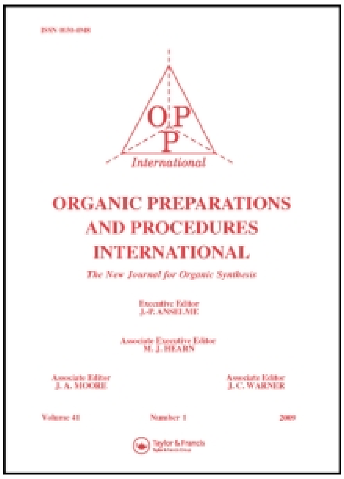

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# A SHORT SYNTHESIS OF TRIDEC-12-EN-2-ONE, THE MINOR CONSTITUENT OF THE BARK OF *LITSEA ELLIPTICA* (LAURACEAE)

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# A SHORT SYNTHESIS OF TRIDEC-12-EN-2-ONE, THE MINOR CONSTITUENT OF THE BARK OF *LITSEA ELLIPTICA* (LAURACEAE)

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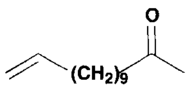
Several plant extracts exhibit diverse biological activities on insects *viz.* insecticidal, juvenile and antijuvenile, moulting hormonal, attractant, repellant etc. Recently, Arbain *et al.*[1] investigated a steam volatile oil obtained from the extraction of the fresh bark of *Litsea elliptica Bl.* tree which is known for its termite resistance and repellant properties. Undec-10-en-2-one (**2**) and tridec-12-en-2-one (**1**) the major and minor components of that volatile oil, were identified[1] by their spectroscopic properties.[1] Compound **1**, one of the defense secretion components of the termite soldiers *Rhinorefines Spp.*,[2] has been synthesized by a lengthy route starting from 11-dodecenal. Herein, we report a facile synthesis of **1** which establishes the structure unequivocally and provide sufficient quantities for biological evaluation.

The bifunctionalty of 10-undecenoic acid (**3**) an easily accessible and inexpensive material, has been explored by us in the synthesis of some natural products[3-5] and prostanoid synthons.[6] Our approach involves yet another example of the usefulness of **3**. LAH reduction of its methyl ester followed by bromination with $PPh_3Br_2$[5,7] resulted in bromide **4**. The latter on reaction with sodium acetylide[7,8] gave enyne **5**; it is to be noted that **5** is also useful as a versatile synthon for the preparation of several insect pheromones.[9] The acetylene function in enyne **5** on hydration in aq. methanol containing catalytic amount of $Hg^{2+}$ ions and $H_2SO_4$[10,11] yielded the title compound **1**. Its physical and spectral data are in agreement with those reported,[1] thus confirming the structure of the natural product.



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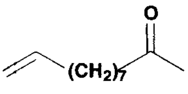

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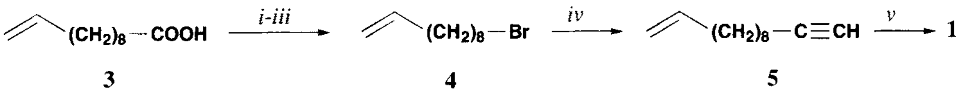

*i*) MeOH, $H^+$ *ii*) LAH, $Et_2O$ *iii*) $Ph_3P$, $Br_2$, $CH_2Cl_2$ *iv*) HC≡CNa/$NH_3$ (l), THF
*v*) cat. $Hg^{2+}$, $H_2SO_4$, aq. MeOH

## EXPERIMENTAL SECTION

The infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer (wave numbers in $cm^{-1}$), $^1H$ and $^{13}C$ NMR spectra were determined in $CDCl_3$ on Brucker AC 200 FT instrument using TMS as internal standard. Chemical shifts are given in ppm (δ scale), coupling constant (J) in Hz. Mass spectra were recorded on Shimadzu QP 1000 A spectrometer operating at 70 ev.

**11-Bromo-1-undecene (4)**.- To triphenylphosphine dibromide[5,7] [from triphenylphosphine (39.6 g, 150 mmol) and bromine (12.0 g, 150 mmol)] in dry methylene chloride was added dropwise a solution of 10-undecenol (25.5 g, 150 mmol)[3-5] and anhydrous pyridine (14 mL) in dry methylene chloride (150 mL). Stirring was continued for further 2 hrs. Most of the solvent was removed *in vacuo* and the residue extracted with hexane. The hexane layer was filtered through a pad (2 inch) of silica gel, concentrated and carefully distilled (frothing !) under reduced pressure to furnish 32.95 g (94%) of the bromide **4**, bp 115°/5 mm Hg, lit.[7] 62°/0.15 mm Hg.

**1-Tridecene-12-yne (5)**.- To a stirred suspension of sodamide in liquid ammonia [prepared from sodium (3.45 g, 0.15 g atom) and liquid ammonia (125 mL)] at -40°, acetylene was bubbled slowly untill the grey suspension became a black solution. Ammonia was slowly evaporated from the reaction mixture and bromide **4** (23.3 g, 100 mmol) in dry THF (150 mL) was added dropwise; the reaction mixture was left overnight at room temperature **without** stirring for the removal of ammonia. The reaction mixture was cooled, quenched with a saturated solution of ammonium chloride, diluted with water and extracted with hexane. The combined hexane extract was washed with dil. HCl (2N), water, brine and dried ($Na_2SO_4$). Removal of the solvent followed by careful distillation under reduced pressure yielded 16.29 g (92%) of the pure alkenyne **5**, bp 78-80°/0.1 mm, lit.[7] bp 55°/0.025 mm Hg; IR (neat): 3320, 3080, 2940, 2880, 2120 (C≡C), 1645 (C=C), 1470, 1440, 990, 910, 720 $cm^{-1}$. $^1H$ NMR (60 MHz, $CDCl_3$): δ 1.35 (bs, 14H, 7x-$CH_2$-), 1.95 (t, 1H, -C≡CH, J = 2.6 Hz), 2.05-2.40 (m, 2H, -$CH_2$-C=C), 4.85-5.30 (m, 2H,-CH=$CH_2$), 5.4-6.30 (m, 1H,-CH=$CH_2$).

**Tridec-12-en-2-one (1)**.- The alkenyne **5** (534 mg, 3 mmol) was added to a mixture of 70% solution of aqueous methanol (5 mL), mercuric sulfate (50 mg) and conc. sulfuric acid (0.01 mL) and kept at 60-70° for 5 hrs. The reaction mixture was cooled, diluted with cold water and extracted with ether.

The combined ethereal extracts were washed with water, brine and dried over anhydrous sodium sulfate. Removal of the solvent followed by column chromatography using neutral alumina (benzene) afforded 302 mg (51%) of **1**, bp 60-65° bath/0.2 mm Hg, lit[1] bp 150°/30 mm Hg; IR (neat): 3080, 2940, 2860, 1725, 1640, 1360, 1165, 990, 910 $cm^{-1}$. $^1H$ NMR (200 MHz, $CDCl_3$): $\delta$ 1.21 (bs, 12H, 6x-$CH_2$-), 1.50 (m, 2H, C4-$H_2$), 1.96 (m, 2H, C11-$H_2$), 2.07 (s, 3H, $CH_3$), 2.36 (t, 2H, C3-$H_2$, J = 7 Hz), 4.86 (br d, 1H, C13-H cisoid, $J_{13,12}$ = 10 Hz), 4.92 br d, 1H, C13-H transoid, $J_{13,12}$ = 17 Hz), 5.70 (ddt, 1H, C12-H, $J_{12,13}$ = 17, 10 Hz, $J_{12,11}$ = 7 Hz). $^{13}C$ NMR (200 MHz, $CDCl_3$): $\delta$ 23.63 (C-8), 28.72 (C-7), 28.93 (C-6 & C-9), 29.18 (C-4, C-5 & C-10), 29.5 (C-1), 33.57 (C-11), 43.50 (C-3), 113.89 (C-13), 138.81 (C-12), 208.61 (C-2). MS m/z (%): 150 (5.2), 149 (36), 139 (6.1), 138 (3.1), 137 (3.7), 125 (9.5), 111 (9.4), 97 (19.4), 96 (23.5), 95 (16.1), 83 (19.5), 82(23.3), 81 (29.1), 71 (92.0), 69 (35.5), 68 (23.4), 67 (33.7), 59 (71.5), 58 (100).

*Anal.* Calcd. for $C_{13}H_{24}O$: C, 79.59; H, 12.24. Found: C, 79.78; H, 12.47

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