Brachylaenalones A and B: Tricyclic Sesquiterpenoid Keto-aldehydes from Heartwood of *Brachylaena hutchinsii* Hutch. (Compositae)

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Summary Partial structures are suggested for two keto-aldehydes isolated from heartwood of *Brachylaena hutchinsii*.

THE East African tree *Brachylaena hutchinsii*, also known as Muhuhu, yields a hard, dense timber used for flooring-blocks.[1] The essential oil obtained by steam-distillation has been characterised in general terms by previous workers.[2] We report the isolation and partial structural determination of two new sesquiterpenoids isolated from the heartwood. Extraction with ethyl acetate gave an oil representing about 20% of the weight of the wood. G.l.c. and g.l.c.–mass spectrometry indicated the presence of numerous compounds, many of which appeared to be of sesquiterpenoid type. Careful chromatography on alumina yielded as principal components a pair of isomeric keto-aldehydes, as well as the apparently analogous keto-alcohols. The keto-aldehydes ("brachylaenolones") were not separated by liquid chromatography but were distinguished by g.l.c.: retention indices for 1% SE-30 at 125° were (A) 1725 (B) 1760. The mass spectra were closely similar, with major ions at m/e 232 (M), 190, 161, 133, and 91. From the mixture of keto-alcohols of retention indices I at 125° (SE-30) 1780 and 1790, respectively, one isomer ($I = 1790$) was isolated with difficulty by t.l.c.: it showed no intense u.v. absorption and had $\nu_{\max}$ (CCl_4) 1720 cm.$^{-1}$. The n.m.r. spectrum indicated a primary allylic alcohol group (τ 5·9, 2H). Sarett oxidation yielded brachylaenalone B.

Borohydride reduction of the mixed brachylaenalones gave a mixture from which three crystalline diols† (a) m.p.

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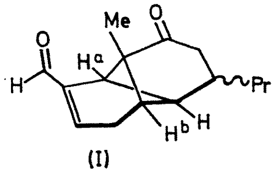
† Considerable variation was observed in optical rotations of samples from different experimental batches, but there was no other evidence of inhomogeneity.

113—114°, (b) m.p. 111—112°, (c) m.p. 141—142°, were isolated by chromatography. The diols were not separable by g.l.c. on SE-30 ($I \sim 1790$ at 125°) but were easily separable by t.l.c. Re-oxidation (Sarett) of diol (a) gave brachylaenalone A,† while diols (b) and (c) each gave brachylaenalone B.† Both compounds were oils, $C_{15}H_{20}O_2$, with similar u.v. and i.r. spectra, *e.g.* isomer A showed $\lambda_{max.}$ (ethanol) 244 nm. (ϵ 9000), $\nu_{max.}$ (CCl_4) 1720, 1688, 1630, 1422, 2810, and 2715 cm.$^{-1}$. Thus the brachylaenalones each contain a saturated ketone and an $\alpha\beta$-unsaturated aldehyde group.

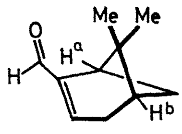
The 100 Mc./sec. n.m.r. spectrum of brachylaenalone A indicated the presence of the following groups: CH_3 on quaternary C (τ9·25), $(CH_3)_2CH$ (9·06 and 9·19, doublets, J 6 c./sec.), CHO (0·49, s). Multiplets at 3·20 (1H), 7·12 (1H), and 7·34 (2H) were consistent with the grouping $\cdot CH_2\cdot CH : C(CHO)CH<$. No further olefinic proton signals were present.

Among known sesquiterpenoid carbon skeletons, only the copaene[3] or ylangene[4,5] type appeared to accommodate the structural elements indicated above. Consideration of the full spectroscopic data led to structure (I)‡ for the brachylaenalones, which are presumed to differ only in the configuration of the isopropyl group. Attempts to correlate the two, by introducing a double bond $\alpha\beta$ to the ketone, have been unsuccessful. Wolff–Kishner reduction of brachylaenalone B gave a complex mixture including a low yield of hydrocarbons; one component resembled α-copaene in its retention on three g.l.c. phases, but identity was by no means certain. We have no reference sample of the closely similar[5] α-ylangene.

Strong support for the structure suggested emerges from the remarkable parallelism between the n.m.r. spectra of the brachylaenalones and the corresponding data for myrtenal (II), which have been analysed in considerable detail.[6,7] The coupling constant of 6·5 c./sec., ascribed to the long-range coupling between the bridgehead protons H^a and H^b in the brachylaenalones, is comparable to those described for analogous protons in myrtenal (5·8 c./sec.),[6,7] α-pinene (5·9 c./sec.)[7] and verbenone (6·5 c./sec.).[7,8]



(I)



(II)

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‡ No assignment of absolute configuration is implied.

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