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COMMENTS ON THE STRUCTURE OF ISOINTERMEDEOL, A SESQUITERPENE REPORTED FROM *CYMBOPOGON FLEXUOSUS*

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Key Word Index—*Cymbopogon flexuosus*; isointermedeol; intermedeol.

Recently Thappa *et al.* [1] described a sesquiterpene alcohol $C_{15}H_{26}O$, isointermedeol, isolated from the essential oil of *Cymbopogon flexuosus*, and have assigned to it the structure and absolute configuration **1**, which corresponds to that of the enantiomer of intermedeol, **2** [2].

Although the spectral properties reported for isointermedeol [1] agree reasonably well with those of intermedeol [2, 3] there are minor differences. The IR spectrum (conditions not specified) of isointermedeol appears to be very similar to that of intermedeol (measured in CCl_4) with the exception that the former contains a band at 805 cm^{-1}, absent from the intermedeol spectrum. All the signals listed for the ^1H NMR spectrum of isointermedeol appear in the spectrum of (+)-intermedeol, recorded under apparently similar conditions. A computer-generated comparison of the MS reported by Thappa *et al.* [1] with that of an authentic sample of intermedeol indicates that with the exception of a peak at m/e 70 (relative abundance 40.0) reported for isointermedeol and absent from the spectrum of intermedeol, the spectra are essentially identical. Measurement of the MS of intermedeol under a variety of conditions failed to provide any evidence of a peak at m/e 70. The mp of isointermedeol is given as 40–41°, whereas that of pure (+)-intermedeol is 47–48°. We have redetermined the specific rotation of an authentic sample of pure, crystalline (+)-intermedeol under the conditions reported by Thappa *et al.* [1] and have found $[\alpha]_D^{25}$ + 10.9°. The specific rotation of +2° reported is not that predicted for the enantiomer of intermedeol.

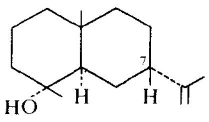
A survey of the literature relating to biosynthetic aspects of eudesmanoid and related bicyclic sesquiterpenes derived from germacrane precursors reveals that, with one exception, levojunenol (**3**), all members of this group isolated from higher plants have a 7β side-chain [4–6]. Andersen [7, 8] has suggested that levojunenol should not be considered a true eudesmanoid sesquiterpene, but that it is related biogenetically to zizanene (**4**) via a plausible biogenetic scheme involving *ent*-β-ylangene (**5**).

On the basis of the above spectral comparisons, the small positive specific rotation of isointermedeol, the somewhat depressed mp of isointermedeol relative to intermedeol, and biosynthetic considerations, we conclude that the material described by Thappa *et al.* [1] is most probably an impure sample of (+)-intermedeol. This conclusion is reinforced by the co-occurrence of normal eudesmanoid sesquiterpenes in *C. flexuosus* [1].

Finally, we should like to comment that if the structure and configuration proposed by Thappa *et al.* [1] prove to be correct, this compound should be named *ent*-intermedeol and not isointermedeol, on the grounds that the prefix 'iso' is generally taken to imply isomerism more deep-seated than a simple enantiometric relationship.

EXPERIMENTAL

Two samples of (+)-intermedeol were available to us. One was kindly provided by Dr. L. H. Zalkow and the other was isolated from the essential oil of a variety of *Bothriochloa intermedia*. Both had mp 47–48°.



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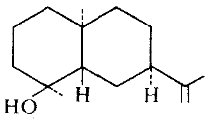

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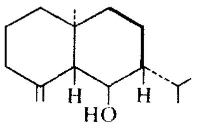

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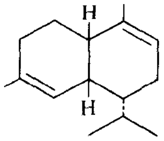

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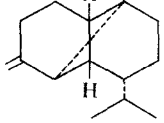

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Acknowledgements—We are indebted to Mr. J. N. Herron for the isolation and purification of intermedeol, and to Mr. R. J. Boston for the mass spectral determinations. Dr. R. M. Ahring (Oklahoma State University) kindly furnished a supply of *B. intermedia*.

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A CARYOPHYLLENE DERIVATIVE FROM *LEUCANTHEMUM MAXIMUM*[*]

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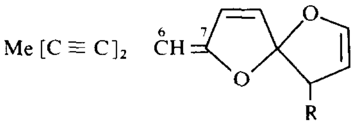
Key Word Index—*Leucanthemum maximum*; Compositae; new caryophyllene derivative.

Investigation of the aerial parts of *Leucanthemum maximum* (Ramond) DC afforded, in addition to the known acetylenes **1**–**7** [1], the lupeol isomer **8** [2], germacrene D and the alcohol **9** [3]. A secondary alcohol was also present. Inspection of the ^{1}H NMR spectral data (Table 1) led to the structure **10**, a 10β-hydroxycaryophyllene. Comparison of the chemical shifts and coupling constants with those of caryophyllene and the observed Eu(fod)$_3$-induced shift showed that we were dealing with a derivative of caryophyllene.

The position of the OH group followed from the change of the 9-H signal, which in caryophyllene derivatives is a typical three-fold doublet and was replaced in the spectrum of **10** by a doublet of doublets. Also the observed Eu(fod)$_3$-induced shifts clearly showed that the *O*-function can only be placed at C-10 (shift of 9-H, 12-H and 15-H). Double resonance experiments supported the assignments. Irradiation of the signal at δ 2.54 (in C_6D_6) collapsed the multiplet at 2.20 to a broadened doublet and the signal at 3.74 to a singlet clearly indicating the assignments of 1-, 9- and 10-H. Irradiation of the methyl singlet at 1.58 collapsed the broadened doublet at 5.33 to a clear double doublet, while saturation of the signal at 1.94 changed the multiplets at 2.35, 1.47 and 1.31. Consequently, we were dealing with the signals of 2-, 2′, 3- and 3′-H. In the ^{1}H NMR spectrum most signals were accompanied by small additional bands, most probably due to a second conformer. Similar observations were made in the case of other caryophyllene derivatives [4].

EXPERIMENTAL

Fresh aerial parts (700 g) (grown from seeds, Botanical Garden Dijon, voucher 79/1397) were extracted with Et_2O–petrol (1:2).



1 R = H (6, 7*E*)
2 R = H (6, 7*Z*)
3 R = OAc (6, 7*E*)
4 R = OH (6, 7*E*)

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[*] Part 273 in the series "Naturally Occurring Terpene Derivatives". For Part 272 see Bohlmann, F. and Lonitz, M. (1980) *Chem. Ber.* **113**, (in press).