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# A EUDESMANEDIOL FROM *CYMBOPOGON DISTANS*

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**Key Word Index**—*Cymbopogon distans*; Gramineae; essential oil; chemotypes; chemical marker; eudesmanediol; X-ray diffraction; absolute configuration.

**Abstract**—[2*R*-(2α,4aβ,8α,8aα)]-Decahydro-8a-hydroxy-α,α,4a,8-tetramethyl-2-naphthalenemethanol, isolated from the essential oil of *Cymbopogon distans*, was studied spectroscopically and identified by means of X-ray diffraction. The absolute configuration was determined based on anomalous scattering from oxygen.

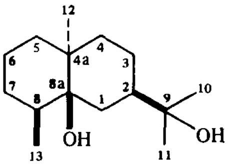
## INTRODUCTION

Screening of aromatic grasses of the Kumaun and Garwhal regions of the Northwest Himalaya has revealed four distinct chemotypes of *Cymbopogon distans* (Steud.) Wats. [1]. The chemical makeup of their essential oils is quite different and each chemotype is characterized by a major component of its essential oil that is not present in the essential oils of the others. These chemical markers are citral, α-oxobisabolene, piperitone and a sesquiterpene diol. We report here the identification of the diol as the previously unreported eudesmanediol **1**.

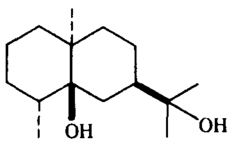
## RESULTS AND DISCUSSION

Compound **1** was isolated by column chromatography of the essential oil. Its EIHR mass spectrum indicated that its molecular formula was $C_{15}H_{28}O_2$ (*m/z* 240.2091; $C_{15}H_{28}O_2$ requires 240.2089). The IR spectrum of **1** indicated the presence of hydroxyl groups and its $^{13}$C NMR spectrum showed that compound **1** is saturated and has one quaternary carbon, two methines, two other tertiary carbons, both of which are bonded to oxygen, six methylenes and four methyls. The $^{1}$H NMR spectrum indicated that two of the methyls are part of a hydroxyisopropyl group and showed that a third methyl is bonded to a methine carbon and that the fourth is bonded to a quaternary carbon. Although comparison of the NMR data for **1** with that recently reported for its diastereomer **2** [2] allows us to assign the structure shown, or its mirror image, to **1** (see below), any ambiguity regarding the structure, including the absolute configuration, was removed by X-ray analysis of crystals obtained by slow evaporation of a solution of **1** in acetone.

Hope and de la Camp [3, 4] have demonstrated that analysis of observed Bijvoet differences due to the anomalous scattering effect of oxygen for Cu$K\alpha$ radiation can be used for the determination of absolute configurations. After preliminary work showed the likelihood that the



**1**



**2**

absolute configuration of **1** could be determined in this way, a crystal was ground to the shape of an oblate spheroid to reduce absorption errors and used to collect both final structure data with MoKα radiation and absolute configuration data.

Bond lengths and bond angles for compound **1** are normal and are given in the supplementary material. Interestingly, crystals of **1** possess an intricate hydrogen-bonding network wherein half of the hydroxyl hydrogens are in one orientation and half in another due to alternation of intra- and inter-molecular hydrogen bonding. The shape of compound **1**, picturing disorder of the hydroxyl hydrogens, is shown in Fig. 1.

A literature search failed to disclose any previous report of compound **1** but did disclose that four of its stereoisomers have been reported [2, 5]. Of these, three were synthesized from γ-eudesmol by sensitized photo-oxygenation followed by treatment with lithium aluminium hydride and then catalytic hydrogenation, and consequently have the 4aα-configuration [5]. The fourth, compound **2**, the C-8 isomer of **1**, was isolated from *Alpinia japonica* and was synthesized from 10-*epi*-γ-eudesmol by a similar sequence except that $(C_6H_5)_3P$ was used in place of lithium aluminium hydride [2]. The 8α-configuration, which is confirmed by our work, was assigned to compound **2**, on the basis of the small pyridine-induced upfield shift of the methyl doublet in the $^1$H NMR spectrum.

The relationship between compounds **1** and **2** can be seen by comparison of their $^{13}$C NMR spectra, which are given in Table 1. The chemical shifts of C-2 to C-4a and C-9 to C-11 are very similar, and the differences in the remaining chemical shifts, particularly those for C-8 and the two other methyl carbons, are completely consistent with those reported for the isomeric 4,10-dimethyl-*trans*-5-decalols [6].

Although we have not yet completed our identification of the other major sesquiterpenes that are formed together with compound **1** by this chemotype of *C. distans*, we have found that 10-*epi*-γ-eudesmol, which we believe is the precursor of **1**, makes up 2.8–3.4% of the essential oil and, by GC/MS, we can place upper limits of 0.05 and 0.3% on the amounts of compound **2** and the structurally related α- and/or β-dihydroagarofuran [7] present in the essential oil.

Table 1. $^{13}$C NMR chemical shifts of compounds **1** and **2** in $CDCl_3$*

| C | 1 | 2 | C | 1 | 2 |
|---|---|---|---|---|---|
| 1 | 29.7 *t* | 31.8 *t* | 8 | 34.7 *d* | 41.2 *d* |
| 2 | 40.8 *d* | 40.2 *d* | 8a | 74.3 *s* | 75.1 *s* |
| 3 | 20.5 *t* | 20.3 *t* | 9 | 73.1 *s* | 72.8 *s* |
| 4 | 34.2 *t* | 34.8 *t* | 10 | 30.6 *q*† | 30.0 *q*† |
| 4a | 36.8 *s* | 36.6 *s* | 11 | 29.5 *q*† | 29.6 *q*† |
| 5 | 34.2 *t* | 36.6 *t* | 12 | 20.1 *q* | 21.8 *q* |
| 6 | 20.75 *t* | 17.0 *t* | 13 | 14.8 *q* | 17.2 *q* |
| 7 | 29.7 *t* | 28.1 *t* | | | |

* Data for compound **2** are from ref. [2].

† These assignments are interchangeable.

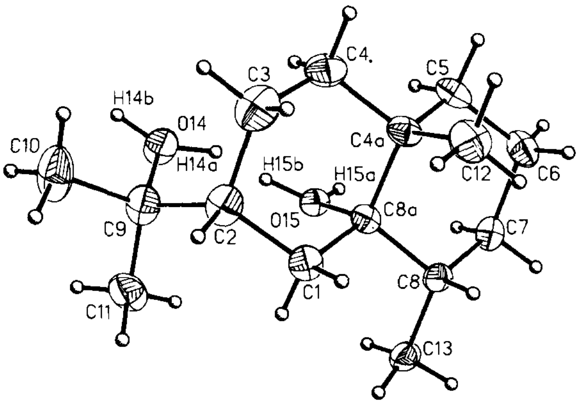


Fig. 1. Computer generated perspective drawing of compound **1**.

## EXPERIMENTAL

*Cymbopogon distans* was collected from Loharkhet, Almora District, elevation 1900 m, in Sept. The identity of the grass was confirmed by J. A. Cope (Kew Gardens) (voucher no. 5H/1865/85).

*Isolation procedure.* The freshly collected grass (800 g) was finely chopped and steam distilled, and the distillate was satd with NaCl and extracted with petrol (bp 40–60°). Concn of the dried $(Na_2SO_4)$ extract by distn at red. pres. left 4 g (0.5%) of oil.

Compound **1** was obtained by CC of the oil on silica gel with hexane–$Et_2O$ (4:1); after recrystallization from $Me_2CO$ it had mp 120–121° (uncorr.), $[\alpha]_D^{25} -9.0°$ ($CHCl_3$, *c* 0.80); MS (70 eV), *m*/*z* (rel. int.): 240.2091 $[M]^+$ (14.7), 222.1959 $[M-H_2O]^+$ (17.5), 207.1728 $[M-CH_5O]^+$ (34.6), 164.1574 $[C_{12}H_{20}]^+$ (54.1), 149.1330 $[C_{11}H_{17}]^+$ (66.5), 126.1029 $[C_8H_{14}O]^+$ (100), 109.1017 $[C_8H_{13}]$ (54.2), 69.0703 $[C_5H_9]^+$ (47.1), 59.0505 $[C_3H_7O]^+$ (59.0). $^{13}$C NMR (50.3 MHz, $CDCl_3$), see Table 1. IR $\nu_{max}^{KBr}$ cm$^{-1}$ (trans. < 50%): 3450, 3310, 2980, 2940, 2870, 1468, 1462, 1450, 1380, 1125, 1000 and 950. $^1$H NMR (360 MHz, $CDCl_3$): $\delta$ 1.254 (*s*, 6H), 1.049, (*s*, 3H) and 0.846 (*d*, $J = 6.63$ Hz, 3H). Found: C, 74.88; H, 11.80. $C_{15}H_{28}O_2$ requires: C, 74.95; H, 11.74%).

*Crystal data.* A prolate spheroidal crystal with axes of 0.43 and 0.75 mm mounted with its long direction close to the $\phi$ axis was used for collection of X-ray data. Determination of cell dimensions and data collection were carried out with the crystal cooled to 130 K on a Syntex $P2_1$ diffractometer using graphite monochromated MoKα radiation ($\lambda = 0.71069$ Å). Crystal data determined using the Syntex $P2_1$ program are: space group $P3_221$ (no. 154); $a = 10.990$ (3), $c = 20.415$ (5) Å, $Z = 6$, $V = 2135.3$ (0.9) Å$^3$, $\mu = 0.67$ cm$^{-1}$ and $d_{calc}$ (130 K) = 1.11 g/cm$^3$. A total of 3777 reflections with $2\theta \leqq 55°$ were measured using the $\omega$-scan mode at 11°/min with a 1° scan range and a ± 1° background offset; index range *h*, 0–13, *k*, 0–13, *l*, −27–27, and two standard reflections were monitored every 198 measurements. No intensity decay was observed during the experiment. There were 1447 independent reflections with $I_0 \geqq 3\sigma(I_0)$ that were judged observed and were used in the solution and refinement of the structure. The crystal structure was solved by direct methods routines of SHELXTL [8]. Block cascade least-squares refine-

Table 2. Observed and calculated relative Bijvoet difference

| (*h*, *k*, *l*) | Equivalent pairs in set | % ratio observed* | % ratio calculated† |
|---|---|---|---|
| 1, 4, 3 | 4 | −6.6 | −5.0 |
| 1, 1, 3 | 6 | 19.5 | 16.6 |
| 2, 3, 5 | 6 | 2.1 | 2.3 |
| 2, 4, 2 | 6 | 3.1 | 2.8 |
| 4, 4, 4 | 6 | −3.5 | −3.9 |
| −11, 7, 8 | 2 | −12.2 | −13.7 |
| 3, 7, 5 | 6 | −13.8 | −9.2 |
| 2, 9, 3 | 6 | 5.0 | 5.5 |
| 6, 6, 3 | 2 | −4.5 | −3.6 |

* $100[2\Sigma F^2(h, k, l)\text{-}\Sigma F^2(\bar{h}, \bar{k}, \bar{l})]/[\Sigma F^2(h, k, l)+\Sigma F^2(\bar{h}, \bar{k}, \bar{l})]$

† $100(2)[(F_{\text{correct}})^2-(F_{\text{mirror}})^2]/[(F_{\text{correct}})^2+(F_{\text{mirror}})^2]$

ment using anisotropic thermal parameters gave final discrepancy indices of $R=0.034$ and $R_w=0.039$. Reflections with optimal Bijvoet differences for CuK$\alpha$ radiation were found with the program ABSCON [4] based on f″ for carbon and oxygen. Bijvoet differences for 9 Friedel pairs, including all 6 intensity equivalent pairs for 6 of the 9 sets,—in all, 88 reflections–were measured. The intensity equivalents were summed, and each sum was treated as an individual reflection and compared with values calculated for the structure shown in Fig. 1 and its mirror image. The data for all sets, which are summarized in Table 2, are in accord with the absolute configuration shown.

Tables of positional and thermal parameters and structure factors are available from the Directory of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. The request should be accompanied by the full literature citation for this report.

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# (+)-α-COPAEN-8-ONE AND OTHER CONSTITUENTS FROM *NEOMIRANDEA* SPECIES

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**Key Word Index**—*Neomirandea angularis*, *N. arthodes*, *N. exima*, *N. guevarii*, *N. parasitica*; Compositae; Eupatorieae; diterpenes; *ent*-clerodanes; sesquiterpenes; copaene derivative; sesquiterpene lactone; heliangolide.

**Abstract**—The investigation of five *Neomirandea* species gave two known *ent*-clerodanes, a heliangolide, a cadinene and a new copaene derivative as well as some widespread compounds.

The genus *Neomirandea* with 27 species is distributed over Central America from Mexico up to Ecuador. It has been placed in the monogeneric subtribe Neomirandiinae [1]. Nothing was known on the chemistry of this genus. We therefore have studied the constituents of five species from Costa Rica. The results are summarized in Table 1.

The aerial parts of *N. angularis* (B. L. Robins.) K. et R. contain in high concentration the *ent*-clerodanes (−) **1** [2] and (−) **2** [3], while those of *N. parasitica* (Klatt.) K. et R. gave the heliangolide (−) **7** [4]. The aerial parts of