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ISOLATION AND CRYSTAL STRUCTURE OF A NOVEL DIHEMIACETAL BIS-MONOTERPENOID FROM *CYMBOPOGON MARTINII*

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Key Word Index—*Cymbopogon martinii*; Gramineae; essential oil; dihemiacetal bis-monoterpenoid; X-ray diffraction; inclusion compound.

Abstract—[2R-(2α, 4aβ, 5aβ, 7α, 9aβ, 10aβ)]-Octahydro-2,7-bis(1-methylethenyl)5a*H*, 10a*H*-4a, 9a-ethanodibenzo[*b*, *e*] [1, 4]dioxin-5a,10a-diol (cymbodiacetal), isolated from the essential oil of *Cymbopogon martinii*, was identified by means of X-ray diffraction of its 1:1 solvate with deuteriochloroform.

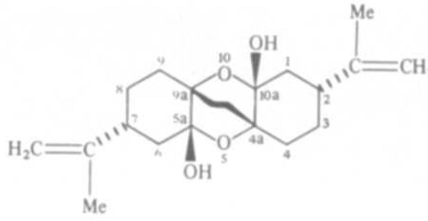
INTRODUCTION

Cymbopogon martinii (Roxb.) Wats. grows wild in many regions of India [1, 2], and several varieties are cultivated commercially as a source of palmarosa or ginger grass oil used in soaps and perfumery [3–5]. We report here the isolation and identification of the novel dihemiacetal bis-monoterpenoid from the essential oil obtained from aerial parts of flowering wild *C. martinii*.

RESULTS AND DISCUSSION

Compound 1 was isolated as a flaky white solid by column chromatography of the essential oil. Its EIHR mass spectrum indicated that its molecular formula is $C_{20}H_{30}O_4$ (*m/z* 334.2135; $C_{20}H_{30}O_4$ requires 334.2144), and its ^{13}C NMR spectrum indicated that it has an element of symmetry (*vide infra*) and possesses O–C–O units. The presence of –OH and $CH_2{=}C$ and the absence of C=O were indicated by its IR spectrum, and its ^1H NMR spectrum indicated the presence of $CH_2{=}C(CH_3)_2$. Slow evaporation of a solution of 1 in $CDCl_3$ gave the 1:1 solvate as crystals suitable for X-ray analysis. The incorporation of one mole of $CDCl_3$ per mole of 1 in the crystal allowed determination of the absolute configuration of 1 with MoKα radiation by measuring the Bijvoet differences [6] for 14 Friedel pairs selected for good observability [7]. All pairs unequivocally indicated the configuration shown as 1 and in Fig. 1. Bond lengths and bond angles obtained for 1 agree well with accepted values. Disregarding the solvent molecule, 1 very closely obeys two-fold symmetry Fig. 1.

A literature search failed to disclose any previous reports of 1 or its logical dihydroxy diketone precursor. Further, the head to head linkage of two monoterpene units present in 1 appears to be unique among natural products so far revealed by Nature. That the R-configuration of C-2 and C-7 in 1 is the same as that in R-(+)-limonene, the major component of the essential oil and the only other so far identified, suggests that 1 may arise from a shunt of the biosynthetic pathway to the monoterpene. A plausible enzyme-moderated reaction that could produce the head to head union is shown in Scheme 1. Conversion of the diterpenoid product shown to 1 requires no novel transformation [8].



1

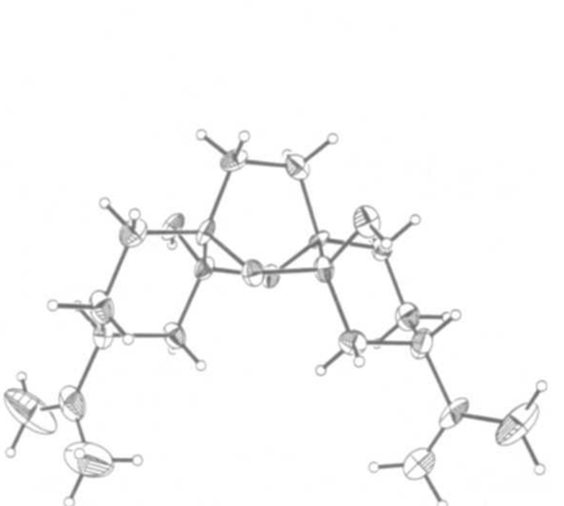
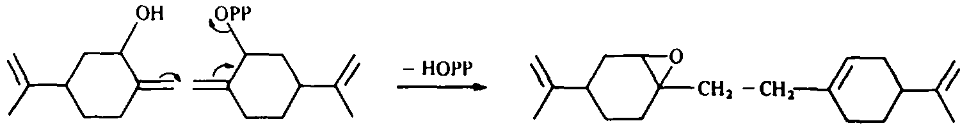


Fig. 1. Computer generated perspective drawing of 1.



Scheme 1

EXPERIMENTAL

Cymbopogon martinii in the flowering stage was collected from Dhaura, Almora District, elevation 1640 m, in September 1982. The identity of the plant was confirmed by P. P. Muyal, Forest Research Institute, Dehra Dun (accession no. 153824) and T. A. Cope and B. M. Wadhwa, Kew Gardens (voucher no. H3/2035/82).

Isolation procedure. The aerial parts (1.75 kg) of the freshly collected plant material were finely chopped and steam distilled, and the distillate was satd with NaCl and extracted with hexane. Concentration of the dried (Na_2SO_4) extract by distillation left 7 ml of pale yellow oil, 4 ml of which was applied to a column prepared from 160 g of 60–120 mesh silica gel and eluted successively with 400 ml hexane, 300 ml hexane–Et_2O (1:1) and 200 ml Et_2O–EtOAc (7:3). Concentration of the hexane fractions yielded *ca* 50 mg of R-(+)-limonene, identified primarily by its rotation, $[\alpha]_D^{25} + 118°$ ($CHCl_3$, *c* 0.4), lit [9] $[\alpha]_D^{20} + 123.2°$ ($CHCl_3$, *c* 1.0), and the excellent agreement of its ^{13}C NMR spectrum with reported spectra of limonene [10]. The mixture obtained by concentration of the hexane–Et_2O fractions remains to be identified. Evaporation of the Et_2O–EtOAc fractions left 6 mg of flaky white solid. Slow evaporation of a soln of the white solid in $CDCl_3$ deposited transparent needles, mp 206–207° (uncorr), $[\alpha]_D^{25} + 26 \pm 5°$ ($CHCl_3$, *c* 0.12), subsequently identified as the 1:1 $CDCl_3$ solvate of **1**.

'*Cymbodiacetal*' (**1**): $CDCl_3$. MS (70 ev), *m/z* (rel. int.): 334.2135 $[M]^+$ (37.1), 316.2031 $[M - H_2O]^+$ (83.3), 298.1936 $[M - 2H_2O]^+$ (30.0), 166.0991 $[C_{10}H_{14}O_2]^+$ (64.2), 107.0859 $[C_8H_{11}]^+$ (100). ^{13}C NMR (50.3 MHz, $CDCl_3$, downfield window to $\delta 120$ ppm), $\delta 108.4$ ($=CH_2$), 97.6 (C-5a), 75.5 (C-4a), 41.3 (C-2 or C-4), 40.8 (C-2 or C-4), 32.9 (C-11), 26.5 (C-1 or C-3), 26.0 (C-1 or C-3) and 20.8 ppm (CH_3). IR, ν_{max} cm^{-1}: 3390 (*s*, OH), 1640 (*w*) and 1080 (*s*, $CH_2=C$). ^1H NMR (360 MHz, $CDCl_3$) $\delta 4.71$ (*br s*, $CH_2=C$), 1.74 (*br s*, $CH_3-C=C$).

Crystal data. A crystal with dimensions 0.65 × 0.17 × 0.12 mm 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 (0.71069 Å). Crystal data determined using the Syntex $P2_1$ diffractometer program are: space group $P2_1$ (No. 4); $a = 5.918$ (3), $b = 17.896$ (9), $c = 10.666$ (10) Å, $\beta = 97.65$ (7)°, $Z = 2$, $V = 1119.5$ (1.4) Å^3, $\mu = 0.70$ cm^{-1} and d_{calc} (130 K) = 0.99 g/cm^3. A total of 2660 independent reflections with $2\theta \leqslant 55°$ were measured using the ω-scan mode at 8°/min with a 1° scan range and a ± 1° background offset; index range *h*, − 7–7, *k*, 0–22, *l*, 0–13, and two standard reflections (020, 110) were monitored every 198 measurements. No intensity decay was observed during the experiment. There were 1660 reflections with $I_0 \geqslant 3\sigma (I_0)$ that were judged observed and were used in the solution and refinement of the structure. The crystal structure was solved by direct methods (11). Block cascade least-squares refinement using anisotropic thermal parameters gave final discrepancy indices of $R = 0.0525$ and $R_w = 0.0557$.

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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