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ISOLATION AND STRUCTURE ELUCIDATION OF A NEW
ISOPIMARANE FROM *PULICARIA WIGHTIANA*¹

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ABSTRACT.—A new isopimarane has been isolated from *Pulicaria wightiana*. It has been characterized as isopimara-8(14),15-diene-7-keto-2 α -ol [**1**] based on spectral data.

Various species of the genus *Pulicaria* (Compositae) are known for their medicinal properties (1). Different classes of natural products such as sesquiterpenoids (2), flavonoids (3), and diterpenoids (4) have been reported from a number of *Pulicaria* species. In this paper, we report the isolation and characterization of a new isopimarane **1** from *Pulicaria wightiana* C.B. Clarke.

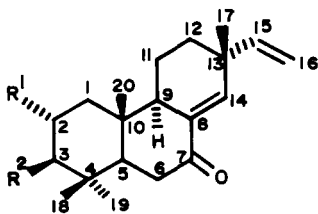
RESULTS AND DISCUSSION

Repeated Si gel cc of the Me₂CO extract of the total plant led to the isolation of **1**, along with β -amyrin acetate and lupeol acetate. Compound **1**, C₂₀H₃₀O₂, [M]⁺ 302, mp 155–157°, [α]_D –9.09, displayed a broad band at 3400 cm⁻¹ and an intense band at 1690 cm⁻¹ in the ir spectrum, indicating the presence of a hydroxyl function and an α,β -unsaturated ketone function. The cisoid nature of the α,β -unsaturated ketone was corroborated by its uv absorption maximum at λ 251 nm (ϵ 2980) (5). The secondary nature of the

hydroxyl group was evidenced by a multiplet centered at δ 3.91 in the ¹H-nmr spectrum of **1** and a shift of the same signal at δ 4.20 in its acetate **2**. The ¹H nmr further exhibited singlets at δ 0.87 (3H), 0.91 (6H), and 1.09 (3H) for four methyls; a doublet at δ 6.71 ($J = 2$ Hz) due to the β proton of an α,β -unsaturated ketone; a multiplet centered at δ 4.98, and a doublet of doublets at δ 5.82 were characteristic signals assignable to a vinyl group. From the above data, it was clear that we were dealing with a diterpenoid with an isopimarane skeleton. The characteristic splitting pattern of vinyl protons confirmed the α orientation of the vinyl group at C-13 (6). A critical comparison of the ¹³C nmr of **1** with that of linifoliol [**3**] (7) confirmed the isopimaradiene skeleton of **1** and the α stereochemistry of H-9 (Table 1). Striking similarity in the ¹H nmr of **1** and **3**, except for chemical shifts of the multiplet due to the carbinyl proton, revealed that **1** was structurally similar to **3** but with a difference in the position of the hydroxyl group. A comparison of the ¹H and ¹³C nmr of **1** with those of isopimara-8(14),15 diene-2 α ,18-diol (**8**) enabled placement of the hydroxyl group at C-2 with α orientation. Observed downfield chemical shifts of C-1 and C-3 in the ¹³C nmr of **1**, about 8 ppm more than normal values (9), confirmed the above assignment.

β -amyrin acetate and lupeol acetate were identified by direct comparison of their physical characteristics and spectral data with those reported (10,11).

In conclusion, the present paper reports the isolation and characterization



- 1** R¹=OH, R²=H
2 R¹=OAc, R²=H
3 R¹=H, R²=OH

¹NCL Communication No. 5302.

TABLE 1. ^{13}C -nmr Data of Compounds 1 and 3.

Carbon	Compound		Carbon	Compound	
	1	3 ^a		1	3
C-1	47.86 t	36.8 t	C-11	19.04 t	19.1 t
C-2	64.87 d	27.3 t	C-12	36.98 t	35.8 t
C-3	50.74 t	78.4 d	C-13	37.61 s	38.6 s
C-4	34.78 s	38.8 s	C-14	144.89 d	144.5 d
C-5	50.97 d	50.6 d	C-15	146.15 d	146.2 d
C-6	33.96 t	34.0 t	C-16	111.79 t	111.2 t
C-7	199.88 co	200.2 co	C-17	25.74 q	25.8 q
C-8	134.58 s	134.7 s	C-18	32.56 q	27.4 q
C-9	49.31 d	49.5 d	C-19	22.00 q	14.6 q
C-10	38.59 s	38.6 s	C-20	14.72 q	13.8 q

^aData for compound 3 are from Mahato and Pal (7).

of isopimara-8(14),15-diene-7-keto-2 α -ol [1].

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—

Melting points are uncorrected. Ir spectra were recorded on a Perkin-Elmer 683 instrument. ^1H - and ^{13}C -nmr spectra were obtained on Bruker WH-90 (Spectrospin) and MSL-300 spectrometers, respectively. Mass spectra were recorded on a Finnigan MAT-1020 operating at 70 eV. Optical rotation was taken on a Jasco DIP-181 digital polarimeter.

EXTRACTION AND ISOLATION.—*P. wightiana*, identified by authorities of the Botanical Survey of India, was collected from Pune, India during October 1988. A voucher specimen has been deposited at the Botanical Survey of India, Pune. The herb was shade-dried and the powdered material (25 kg) extracted with Me_2CO . The total extract (65 gm) was subjected to Si gel (60–120 mesh) chromatography using Me_2CO /petroleum ether as eluent with increasing polarity. Three major fractions, A (25 g), B (10 g), and C (27 g), were collected.

Fraction B (10 g) on cc using $\text{EtOAc}/\text{C}_6\text{H}_6$ as an elution gradient and repeated preparative tlc separation with Si gel (100–200 mesh) yielded compound 1 (9 mg), mp 155–157° (MeOH), $[\alpha]^{23}_{\text{D}} -9.09$ ($c=0.07$, CHCl_3); uv λ max (MeOH) 251 nm (ϵ 2980); ir (CHCl_3) ν max 3400, 1690, 1620 cm^{-1} ; ^1H nmr (90 MHz, CDCl_3) δ 0.87 (s, Me-20), 0.91 (s, Me-18, -19), 1.09 (s, Me-17), 3.91 (m, H-2), 4.98 (m, H-16), 5.82 (dd, $J=10$, 18 Hz, H-15), 6.71 (d, $J=2$ Hz, H-14), δ 1.23 (m), 1.54 (m), 2.15 (m), 2.44 (m), 2.67 (m); ^{13}C nmr (300 MHz, CDCl_3) see Table 1; eims, m/z (%) 302 (100), 284 (37), 274 (7), 269 (38), 202 (62).

The acetylation of 1 with pyridine/ Ac_2O at room temperature yielded 2, a gummy solid: ir

(CHCl_3) ν max 1730, 1682, 1612, 1216 cm^{-1} ; ^1H nmr (80 MHz, CDCl_3) δ 0.92 (s, Me-18, -19), 1.00 (s, Me-20), 1.1 (s, Me-17), 2.04 (s, OCOMe), 4.20 (m, H-2), 4.99 (m, H-16), 5.84 (dd, $J=10$ Hz, 18 Hz, H-15), 6.80 (d, $J=2$ Hz, H-14).

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