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SESQUITERPENES FROM *PEREZIA LONGIFOLIA*

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In earlier communications (1,2) we described the iolation of some terpenoids from *Perezia carpholepis* and *Perezia alamani* var. *oolepis*. Among others, cyperene [**2**], parvifoline [**1a**], and diperezone were found. We have now completed the study of another related plant, *Perezia longifolia* Blake (Compositae) from which cyperene [**2**], α-curcumene [**3**], and parvifoline [**1a**] in important yields were isolated in addition to parvifoline isovalerate [**1b**].

Hexane extraction of the roots of *P. longifolia* yielded a reddish oil. ^{1}H nmr of the crude mixture gave evidence of the presence of parvifoline [**1a**] besides some other minor components. Column chromatography gave three major fractions, and tlc gave two compounds from the less polar fraction, one from the intermediate, and one from the most polar.

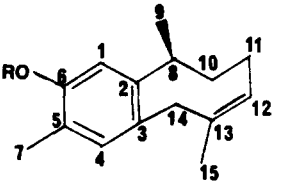
The physical and spectroscopic properties of the two oils obtained from the less polar fractions indicated these compounds to be cyperene [**2**] (1) and α-curcumene [**3**] (3).

The intermediate polarity fractions were rechromatographed to yield a homogeneous, colorless oil. ^{1}H-nmr analysis showed resonances typical of parvifoline [**1a**] and additional signals centered at 2.5 and 1.32 ppm. Ir spectroscopy showed a bond corresponding to an enol ester. The spectroscopic data suggested that the compound was the isovaleryl ester of parvifoline [**1b**]. Definitive proof of this structure was obtained by alkaline hydrolysis, which produced parvifoline [**1a**], identified by comparison with an authentic sample (1), and isovaleric acid, characterized by its spectroscopic properties and by comparison of the corresponding anilide derivative (4) with an authentic sample.

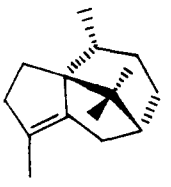
The structural assignment of parvifoline [**1a**] to the most polar and most abundant compound (15% of dried root weight) was made by direct comparison with an authentic sample (1).

EXPERIMENTAL

EXTRACTION OF *P. LONGIFOLIA*.—The dried, ground roots (100 g) of *P. longifolia* (collected near Zamora, Michoacán in July 1986; voucher samples were deposited at the Escuela de Biología, Universidad Michoacana, Morelia



1a R=H
1b R=iVal



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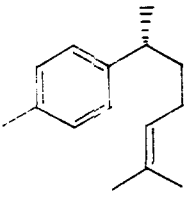

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Mich., México) were extracted three times with 2 liters of hexane under reflux for 5 h. The combined extracts were evaporated to dryness, and the residue (16 g) was chromatographed over 1000 g of Si gel with solvents of increasing polarity. Three main fractions were separated: A (pentane/hexane), B (hexane/C_6H_6), and C (C_6H_6). The less polar fraction A gave a colorless oil (380 mg), which gave two compounds on tlc. Further chromatography using pentane and pentane/hexane provided pure compounds cyperene [**2**] and α-curcumene [**3**], which were identical in all respects with authentic samples.

PARVIFOLINE ISOVALERATE [**1b**].—Fraction B was rechromatographed over SiO_2 using hexane-C_6H_6 (8:2) to give 600 mg of parvifoline isovalerate [**1b**] as a colorless oil; uv λ max (EtOH) 230 and 275 nm (ε 13800 and 7500); ir ν max cm^{-1} 1780 (phenol ester), 1650 and 1520 (C=C, double bonds); ^1H nmr 6.73 and 6.40 (s, H4, H1), 5.2 (t with unresolved couplings $J=7$ Hz, H12), 3.5 and 3.3 (2d, $J=18$ Hz, 1H each, H14 and 14′), 3.01 (m, 2H, H8 and H3′), 2.49 (s br, 2H, Hs2′), 2.10 (s aromatic Me), 1.66 (s br, 3H, vinylic methyl), 1.14 (d, $J=7$ Hz 3H secondary methyl) and 1.05 (d, $J=7$ Hz, 6H isovaleryl methyls); ms *m/z* 300 ($M^{+\cdot}$), 215 (M-$C_5H_9O)^{+\cdot}$ and 85 $(C_5H_9O)^{+\cdot}$.

HYDROLYSIS OF ISOVALERYL PARVIFOLINE [**1b**].—A solution of 100 mg of the ester in 5 ml EtOH containing 1 ml 10% NaOH was cooled and stirred for 15 min. The mixture was neutralized with 5% HCl, extracted with Et_2O, dried, and evaporated. Crystallization from Me_2CO/hexane afforded parvifoline [**1a**] identified with an authentic sample by standard procedures. The mother liquors were acidified and extracted with Et_2O to yield isovaleric acid which was heated with $SOCl_2$ (50 mg) and added to 70 mg of aniline to give isovaleryl anilide, identified by comparison with an authentical sample.

PARVIFOLINE [**1a**].—Fraction C was evaporated to dryness yielding 15 g of a white solid which was recrystallized from Me_2CO/hexane to yield 14.9 g of parvifoline [**1a**] mp 89-90°, identical with an authentic sample.

ACKNOWLEDGMENTS

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