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LEUCOXOL, A NEW DITERPENOID FROM *ACACIA LEUCOPHLOEA*. X-RAY STRUCTURE DETERMINATION

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Abstract- From *Acacia leucophloea* (Roxb.) Willd. (Mimosaceae) the new diterpenoid 11α, 16-epoxy-1β, 15*R*-dihydroxy-isopimar-8(14)-ene (leucoxol) has been isolated. Its structure was determined by X-ray diffraction analysis.

In a previous communication[1] we reported the structures of leucophleol [1β, 15*R*, 16-trihydroxy-pimar-8(14)-ene] and leucophleoxol [15*R*, 16-epoxy-1β, 11α-dihydroxy-pimar-8(14)-ene], isolated from the root bark of *Acacia leucophloea*, an indian plant used in indigenous medicine. Now another diterpenoid, leucoxol (1), has been isolated from the same source.

Leucoxol (1)[2] [$C_{20}H_{32}O_3$, mp 222.5-224° (EtOAc-*n*-hexane); $[\alpha]_D^{20°}$ -102.0° (*c* 0.48, EtOH)] showed strong OH absorption (3405, 3320 cm^{-1}) and no CO bands. On acetylation compound 1 gave a diacetate [2, a syrup, $[\alpha]_D^{20°}$ -47.6° (*c* 0.47, $CHCl_3$)] the IR spectrum of which was devoid of OH absorptions. It seemed plausible that the third oxygen atom was involved in an ether linkage.

On the other hand ^1H and ^{13}C NMR spectra of the diacetyl derivative were in agreement with structure 2 for leucoxol diacetate [^1H NMR (δ): 5.37 (1H, br *s*, $W_{1/2}$ = 4.5 Hz, H-14), 4.80 (1H, *q*, $J_{aa'}$ = 10 Hz, $J_{ae'}$ = 5.5 Hz, H-1), 4.70 (1H, X part of an ABX system, J_{XA} = 11 Hz, J_{XB} = 5.5 Hz, H-15), 4.46 (1H, *m*, $W_{1/2}$ = 7 Hz, H-11), 3.62 (1H, B part, J_{AB} = 11 Hz, H-16), 3.10 (1H, A part, H'-16), 2.04 and 2.01 (3H each, *s*, two -OAc), C-Me *s* at 1.00, 0.92, 0.90 and 0.85. ^{13}C NMR ppm (carbon No.): 75.8 (1), 25.6 (2), 39.1 (3), 33.4 (4), 54.6 (5), 22.4 (6), 36.1 (7), 140.2 (8), 54.9 (9), 43.0 (10), 68.3 (11), 37.6 (12), 32.5 (13), 127.4 (14), 81.9 (15), 60.9 (16), 24.8 (17), 33.4 (18), 21.9 (19), 11.5 (20), two -OAc at 170.3, 169.8, 21.6 and 20.8].

Leucoxol (1) crystallizes in the space group C2, Z=4, with a=23.569(1), b=8.3320(2), c=9.7529(2) Å, β=110.46(1)° and D_c=1.1862 g.cm^{-3}. Intensities of 1648 independent Friedel pairs were alternately collected in the range $2° \leqslant \theta \leqslant 65°$ on a computer-controlled diffractometer. Graphite-monochromated CuK$_\alpha$ radiation (1.5418 Å) was used. No crystal decom

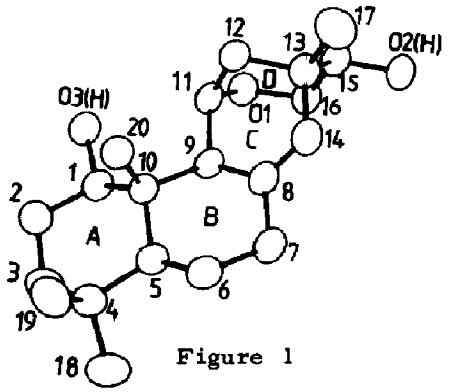
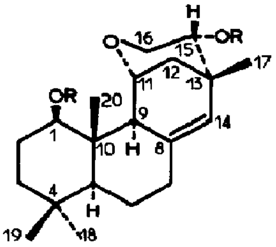


Figure 1



1 R = H

2 R = Ac

position was observed during th data collection process. After t usual correction for Lorentz an polarization effects, 1458 Fried pairs were considered as obser according to the criterion $I>2\sigma($ and were used in the calculatio The structure was solved by di methods[4]. The hydrogen atoms were located on a difference Fo rier map. A convenient weighting scheme[5] was selected to prevent bias in $<w\Delta^2F>$ vs. $<|F_o|>$ and $<\sin\theta/\lambda>$. Several cycles of weighted anisotropic refinement (fixed isotropic thermal parameters for H atoms) including both hkl and $\overline{hkl}$ reflections gave for the rig enantiomer the following unweighted and weighted discrepancy indices: R=0.040 and R_w = 0.056. The absolute configuration was confirmed by comparing the 78 more relevant Bijvoet pairs, giving the following discrepancy indices[6]: average Bijvoet difference $R_1 = \Sigma\left|\left[F_o(+h)-F_o(-h)\right]-\left[F_c(+h)-F_c(-h)\right]\right|/N = 0.287$ (0.383 for the reversal enantiomorph), ave ge Bijvoet ratio $R_2 = \Sigma|R_o-R_c|/N = 0.030$ (0.041) and $R_3 = \Sigma|\Delta I_o-\Delta I_c|/\Sigma|\Delta I_o| = 0.923$ (1.156) w $N = 78$, $R_o = \Delta I_o/<F_o^2>$, $R_c = \Delta I_c/<F_c^2>$, $\Delta I_o = F_o^2(+h)-F_o^2(-h)$, and $\Delta I_c = F_c^2(+h)-F_c^2(-h)$. Fig. 1 shows the absolute configuration of the final X-ray model. Ring A presents a cha conformation having C(1) and C(4) at -0.68 Å and 0.61 Å respectively out of the best pla defined by C(2)-C(3)-C(5)-C(10) with atomic deviations from the plane $\delta < 0.008$ Å. Ring shows also a chair conformation with C(5) and C(8) at 0.71 and -0.59 Å respectively out the best plane defined by C(6)-C(7)-C(9)-C(10), $\delta < 0.015$ Å. Ring C is forced by the dou bond C(8)=C(14) to be envelop conformated, C(12) being at 0.70 Å from the best plane d ed by C(8)-C(9)-C(11)-C(13)-C(14), $\delta < 0.010$ Å. Ring D shows a chair conformation, the best plane being defined by 0(1)-C(11)-C(13)-C(15), $\delta < 0.025$ Å, with C(12) and C(16) at -0.74 and 0.61 Å out of the plane. The molecules are linked by the intermolecular hydr gen bonds, 0(2)... 0(3)H = 2.80 Å and 0(1)... 0 (2)H = 2.77 Å.

Would leucoxol arise from leucophleoxol by attack of the 11α-OH to the 15R, 16-o rane ring, the C-13 stereochemistry of the previously described diterpenoids (leucophle and leucophleoxol)[1] may be reversed on biogenetic reasons.

REFERENCES AND NOTE

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