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THE ISOLATION AND MOLECULAR STRUCTURE OF LUPEOL β-PHENYLPROPIONATE FROM *CNIDOSCULOS ELASTICUS*

PORFIRIO CABALLERO, FRANK R. FRONCZEK, NIKOLAUS H. FISCHER,

Department of Chemistry, Louisiana State University, Baton Rouge, LA 70803

SALVADOR FERNANDEZ, and EDGARDO HERNANDEZ

Centro de Investigacion en Quimica Aplicada, Saltillo, Coahuila, Mexico

ABSTRACT.—The isolation and structure determination of a new triterpene, lupeol β-phenylpropionate from *Cnidosculos elasticus* is reported. The structure was inferred from spectral data and the molecular structure of lupeol β-phenylpropionate was determined by single crystal X-ray diffraction.

Cnidosculos elasticus Lundell (Euphorbiaceae), known in Mexico as *chilte*, is a small rubber-producing tree found in western Mexico. One of the nondesirable mechanical properties of the crude latex of *chilte* is its low elasticity, which is caused by the presence of extractable lipids (fats and triterpenoïds). Soxhlet-extraction of the crude latex with Me_2CO gave a colorless solid material. Column chromatography on silica gel using a hexane-toluene mixture (1:2) as eluant provided in early fractions fatty material (nmr, ms) followed by the known lupeol cinnamate (**3**) (1), a new triterpenoid, and lupeol acetate (**2**) (1). This paper describes the structure determination of the new lupeol ester by nmr, mass spectral methods, and single-crystal X-ray diffraction.

RESULTS AND DISCUSSION

The skeleton of the molecule was unambiguously determined by the X-ray determination to be that of lupeol, containing four six-membered rings and one five-membered ring, all *trans*-fused. The molecule is illustrated in Figure 1, in which all six-membered rings are seen to have the chair conformation. The sole skeletal unsaturation is the terminal double bond C20=C29 [1.334(13)Å], which shows no evidence of disorder with the single bond C20-C30. The 33 single bonds of the lupeol skeleton range from 1.499(10) to 1.583(9)Å in length and average 1.545Å. In the structure determination of the closely related triterpene 3β-acetoxy-20-hydroxylupane (2), corresponding values were found to be more variable, 1.460(14)-1.643(11)Å, and to average 1.551Å. Skeletal bond angles are normal, averaging 111.0° within six-membered rings and 103.5° within the five-membered ring. In 3β-acetoxy-20-hydroxylupane, corresponding averages are 110.9° and 103.7°, respectively. The five-membered ring of lupeol β-phenylpropionate is puckered into a conformation resembling the half-chair, with C21 on the pseudo-twofold axis. Internal torsion angles about its bonds are C17-C18, −47.7°; C18-C19, 34.6°; C19-C21, −9.6°; C21-C22, −19.6°; and C22-C17, 40.4°.

EXPERIMENTAL

CHEMICAL DATA.—Latex of *C. elasticus* was collected from plants in the state of Sinaloa, Mexico. The latex was coagulated by exposure to air, and 115 g were cut into small pieces and extracted with Me_2CO in a Soxhlet extractor. The extraction resulted in 54 g of an Me_2CO-extractable white solid, which was composed of four major constituents, as indicated by tlc on silica gel (hexane-toluene; 1:2; Rf 0.88, 0.63, 0.56, and 0.36). Column chromatography on silica gel using hexane-toluene (1:2) as an eluent provided in early fractions fatty lipids (nmr, ms) that represented 27% of the total Me_2CO extract. Subsequent fractions contained 25% of the known lupeol cinnamate (**3**) (1), followed by lupeol β-phenylpropionate (**4** (23% of total Me_2CO extract), which was recrystallized from Me_2OH to give colorless crystals, mp 211°, used for single crystal X-ray diffraction studies. Later fractions contained 25% of lupeol acetate (**2**) (1). The

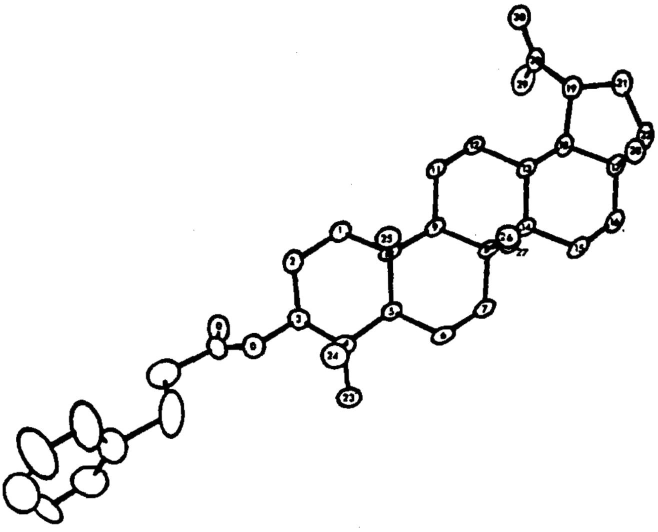


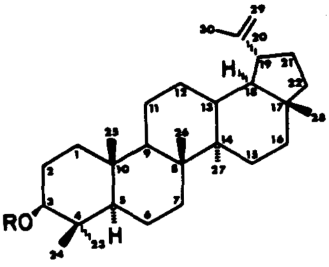
FIGURE 1. Molecular structure of lupeol β-phenylpropionate.

identity of compounds **2** and **3** was established by nmr and ms comparison with data described in the literature (1).

LUPEOL β-PHENYLPROPIONATE (**4**).—$C_{39}H_{58}O_2$, mp 211° (MeOH); *ir*, 1730 (ester), 1645 (double bonds), 1250 (ester) cm^{-1}; hrms, 70 eV, *m/z* (rel. int.), 558.4436 (18.5, M^+) 408.3760 (8.6, M-**A**^{1}) 150.0680 (5.6, **A**^{1}) 133.0632 (11.8, **A**^{2}) 105.0761 (100, **A**^{3}); pmr, δ 7.2 (5H, aromatic), 4.68 brd (H-29a, *J*=2.5 Hz), 4.57 m (H-29b), 4.47 dd (H-3, *J*=10, 6Hz), 2.96 br dd (2H-3′, 8Hz), 2.63 dd (2 H-2′, *J*=6.5, 8.5Hz, 2.38 br ddd (H-19, *J*=5.5, 11, 11), 1.68 brs (3H, C-20-Me), 0.93, 0.84, 0.74, 0.71, 0.68, 0.67 (6 x 3H, methyls).

Anal. calcd for $C_{39}H_{58}O_2$: 558.4436. Found (ms) 558.4393.

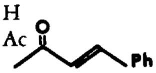
X-RAY DATA.—A crystal of dimensions 0.20×0.36×0.40 mm was used for data collection on an Enraf-Nonius CAD4 diffractometer equipped with CuKα radiation (λ=1.54184Å) and a graphite monochromator. Crystal data are: $C_{39}H_{58}O_2$, MW=558.9, monoclinic space group C2, *a*=36.627(9), *b*=11.260(3), *c*=8.152(2)Å, β=95.68(2)°, Z=4, d_c=1.110 g cm^{-3}, μ(CuKα)=5.06 cm^{-1}. Intensity data were measured by ω-2θ scans of variable speed, designed to yield I≃25σ(I) for all significant data. All data in one quadrant having h+k even and 2°<θ<60° were measured, yielding 1708 reflections for which



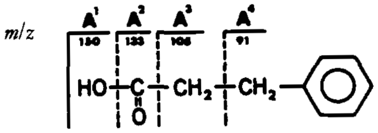
1 R=H

2 R=Ac

3 R=



4 R=



F>3σ(F), which were used in the refinement. Data reduction included corrections for background, Lorentz, and polarization effects; absorption effects were insignificant.

The structure was solved by direct methods, utilizing program MULTAN 78 (3). From the initial E map, 34 atomic positions were assigned, of which 29 proved to be correct. The structure was completed by Fourier techniques.

The region of the β-phenylpropionate substituent afforded some difficulty, the positions of the α and β carbon atoms being ill defined and apparently disordered. These atoms were represented by single positions with large thermal parameters for refinement purposes. Although refinement resulted in unsatisfactory geometry for this substituent, the lupeol skeleton is not affected.

Refinement was carried out by full-matrix least squares with unit weights, treating nonhydrogen atoms anisotropically. Most hydrogen atom positions could be discerned from difference maps; however, all but those of methyl group C30 were placed in calculated positions. Those on C30 were placed from maps. All H atoms were included as fixed contributions to the structure factors and were not refined. Convergence was achieved with R=0.069 and a maximum residual of 0.18eÅ^{-3}, in the region of the ester substituent. Final coordinates for nonhydrogen atoms are given in Table 1.

TABLE 1. Coordinates for Nonhydrogen Atoms, Lupeol β-Phenylpropionate

Atom	x	y	z	Atom	x	y	z
O1	0.6399(2)[a]	0	0.0657(7)	C20	0.9412(2)	−0.0326(13)	−0.0645(10)
O2	0.6501(2)	0.1294(7)	0.2791(8)	C21	0.9588(3)	−0.0167(14)	−0.3563(11)
C1	0.7418(2)	−0.0556(8)	0.0618(9)	C22	0.9389(3)	0.0504(11)	−0.5076(10)
C2	0.7028(2)	−0.0670(9)	0.1111(10)	C23	0.6537(3)	0.1165(10)	−0.2440(11)
C3	0.6766(2)	0.0191(8)	0.0157(9)	C24	0.6532(3)	−0.1089(11)	−0.2278(12)
C4	0.6747(2)	0.0052(9)	−0.1692(9)	C25	0.7357(3)	−0.2102(8)	−0.1642(11)
C5	0.7150(2)	0.0119(8)	−0.2185(8)	C26	0.7864(2)	−0.1525(9)	−0.4439(10)
C6	0.7176(2)	0.0070(9)	−0.4081(9)	C27	0.8260(3)	0.1642(9)	−0.3115(11)
C7	0.7550(3)	0.0473(8)	−0.4442(9)	C28	0.8966(3)	−0.1201(10)	−0.5861(10)
C8	0.7876(2)	−0.0259(8)	−0.3607(8)	C29	0.9521(3)	−0.1236(15)	0.0330(11)
C9	0.7820(2)	−0.0363(7)	−0.1731(8)	C30	0.9423(4)	0.0943(13)	−0.0088(13)
C10	0.7431(2)	−0.0759(7)	−0.1291(8)	C31	0.6307(2)	0.0595(10)	0.1978(12)
C11	0.8141(2)	−0.1041(9)	−0.0820(9)	C32	0.5914(3)	0.030(2)	0.262(2)
C12	0.8517(2)	−0.0522(9)	−0.1037(9)	C33	0.5685(5)	0.020(3)	0.144(2)
C13	0.8569(2)	−0.0394(8)	−0.2912(8)	C34	0.5258(4)	0.002(2)	0.218(2)
C14	0.8254(2)	0.0378(8)	−0.3818(9)	C35	0.5196(5)	−0.127(2)	0.250(2)
C15	0.8326(3)	0.0516(9)	−0.5662(9)	C36	0.4851(5)	−0.149(2)	0.300(3)
C16	0.8707(3)	0.0907(10)	−0.5923(10)	C37	0.4610(4)	−0.071(4)	0.303(2)
C17	0.8999(2)	0.0074(10)	−0.5104(9)	C38	0.4684(3)	0.072(3)	0.293(2)
C18	0.8947(2)	0.0064(10)	−0.3230(9)	C39	0.5027(5)	0.103(2)	0.259(2)
C19	0.9295(2)	−0.0579(10)	−0.2463(10)				

[a] Estimated standard deviations in the least significant digits are shown in parentheses

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