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GYMNOSPERMIN A NEW LABDAN TRIOL FROM *GYMNOSPERMA GLUTINOSA*

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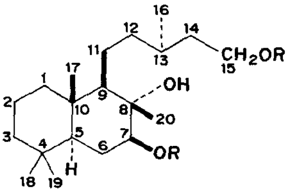
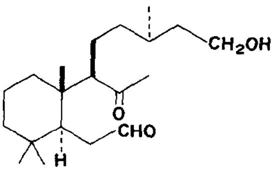
Key Word Index—*Gymnosperma glutinosa*, Compositae, diterpene, gymnospermin, labdan triol

Abstract—The structure of *gymnospermin* (**1**), a new diterpene triol isolated from a collection of *Gymnosperma glutinosa* (Compositae) from Mexico, has been determined to be (−)-7β,8α,15-trihydroxy-labdan

A chloroform extract of *Gymnosperma glutinosa* collected in 1970 near Linares, Mexico, afforded a new crystalline diterpene triol, $C_{20}H_{38}O_3$, $[\alpha]_D^{21}$ −8 3°, which we named gymnospermin (**1**)



(**1**) R = H
(**2**) R = Ac



(**3**)

IR and NMR spectral properties of gymnospermin (**1**) and two essential derivatives, i e a diacetate (**2**) and a hydroxyketo-aldehyde (**3**) obtained by periodic oxidation of (**1**), were indicative of a labdan skeleton containing a 7,8-diol function and a primary hydroxy group

Except for having the opposite optical rotation, the identity of gymnospermin with known (+)-7α,8β,15-trihydroxy-*enantio*-labdan[1] was established by direct comparison[2] IR, NMR and m p , thus, gymnospermin is the enantiomeric of the known triol and can also be represented by structure (**1**)

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[1] The compound was derived from the corresponding 15-oic acid from *Dodonaes lobulata*, Dawson R M Jarvis, M W Jefferies, P R Payne T G and Rosich R S (1966) *Australian J Chem* **19**, 2133

[2] We are thankful to Dr P R Jefferies for an authentic specimen of (+)-7α,8β,15-trihydroxy-*enantio*-labdan ($[\alpha]_D^{20}$ + 6°, c 0 63, $CHCl_3$), m p 148–148 5°

EXPERIMENTAL*

Isolation of gymnospermin (**1**) *from* Gymnosperma glutinosa. Dried and ground plant material (300 g) of *Gymnosperma glutinosa* collected July 1970, about 30 km south of Linares, Mexico, was extracted with $CHCl_3$ and worked-up in the usual way,[3] yielded of crude syrup 25.5 g. Trituration of the crude syrup with Et_2O yielded 3.5 g of crude crystals which afforded 2.0 g of pure gymnospermin (**1**) after recrystallization from C_6H_6 and EtOAc, m.p. 148–148.5°, $[\alpha]_D^{21}$ −8.3 (*c* 0.65, $CHCl_3$) (Found: C, 73.10; H, 11.86. $C_{20}H_{38}O_3$ requires C, 73.57; H, 11.73%). IR (Nujol): 3450 cm^{-1} (OH). NMR: 3.45–3.80 (*m*, 3H) for 7α-H and CH_2OH, 1.11 (*s*, 3H) for tert. Me, 0.88 (*s*, 3H) for tert. Me and 0.80 (*s*, 6H) for two tert. Me.

Gymnospermin diacetate (**2**) (Pyridine–Ac_2O) was purified on silica gel TLC with C_6H_6–ethyl acetate (1:1) (R_f 0.60) giving (**2**) as an oil. MS: M^+ 410. IR (neat): 3550 cm^{-1} (OH), 1735 and 1240 (acetyl). NMR: 4.54–4.90 (*m*[4], 1H) for 7α-H, 4.08 (*t*, *J* 6.5 Hz, 2H) for $-CH_2OAc$, 2.07 and 2.02 (*s*, 3H for each) for acetyl Me, 1.13 (*s*, 3H) for tert. Me, 0.88 (*s*, 3H) for tert. Me and 0.81 (*s*, 6H) for two tert. Me.

Hydroxy-keto-aldehyde (**3**). Gymnospermin was oxidized in tetrahydrofuran with HIO_4 for 5 min at room temp. The mixture was diluted with H_2O and extracted with 3 × Et_2O and dried (Na_2SO_4). Purification on silica gel TLC with C_6H_6–acetone (7:3) (R_f 0.35) gave (**3**) as an oil. IR (neat): 3500 cm^{-1} (OH), 2750 and 1725 (aldehyde) and 1715 (ketone). NMR: 9.77 (*t*, *J* 2 Hz, 1H) for CH_2CHO, 3.62 (*t*, *J* 6 Hz, 2H) for CH_2OH, 2.44 (*dd*, *J* 5, 2 Hz, 2H) for $-CH_2CHO$, 2.12 (*s*, 3H) for $-COCH_3$, 0.91 (*s*, 6H) for two tert. Me and 0.82 (*s*, 3H) for tert. Me.

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* All m.ps are uncorrected. NMR spectra were recorded in $CDCl_3$ on a Hitachi R-20B (60 MHz) spectrometer at 35°. Values are given in ppm (δ-scale) relative to TMS as an internal standard.

[3] MABRY, T. J., MILLER, H. E., KAGAN, H. B. and RENOLD, W. (1966) *Tetrahedron* **22**, 1142.

[4] The 7α-proton signal was observed as a second order multiplet on a 60 MHz spectrometer. When recorded on a 90 MHz spectrometer (Hitachi R-22) this proton signal turned up as a first order quartet. We are thankful to Drs E. L. Ghisalberti and K. Tori for many helpful discussions and to Prof. K. Koshimizu for the 90 MHz NMR analyses.