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CONSTITUENTS OF *Pluchea sericea*. STRUCTURE AND STEREOCHEMISTRY OF (11S)-11,13-DIHYDROTESSARIC ACID[1,2,3]

Alfonso ROMO DE VIVAR*, Benito REYES, Guillermo DELGADO
and Elmer O. SCHLEMPER +

Instituto de Química de la Universidad Nacional Autónoma de México,
Circuito Exterior, Ciudad Universitaria, Coyoacán, 04510 México, D.F.

+ Department of Chemistry, University of Missouri-Columbia,
Columbia, Missouri 65211, U. S. A.

A chemical investigation of *Pluchea sericea* (Inuleae, Compositae) afforded the new sesquiterpene, (11S)-11,13-dihydrotessaric acid (7), in addition to tessaric acid (6), quercetin-3,3'-dimethyl ether (5) and taraxasteryl acetate (4). The structure of the acid (7) was elucidated by chemical transformations as well as spectroscopic methods and X-ray diffraction analysis.

The genus *Pluchea* comprises 40 species,[4] some of them have been studied chemically and shown to contain a variety of sesquiterpene derivatives with eudesmane skeleton such as cuauhtemone (1),[5] plucheinol (2)[6] and pluchea lactone (3).[7]

During the course of our systematic investigation of the mexican Compositae we have found in *Pluchea sericea* a new eremophilanic acid and several known substances, none of them being eudesmane derivatives as those found in the previously studied *Pluchea* species.[8]

The chloroformic extract of *Pluchea sericea* was extensively chromatographed on silica gel to afford, in order of increasing polarity, taraxasteryl acetate (4), quercetin-3,3'-dimethyl ether (5), tessaric acid (6) and the new sesquiterpene (11S)-11,13-dihydrotessaric acid (7).

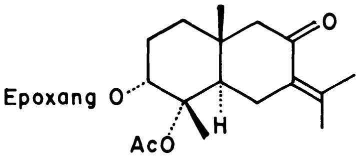
Taraxasteryl acetate (4, 0.15%, mp 255-6°C, lit.[10] : 256-7°C) and quercetin-3,3'-dimethyl ether (5, 0.005%, mp 254-6°C, lit.[11]: 256-60°C) were identified by their spectroscopic characteristics[12] and direct comparison with authentic samples.

Tessaric acid (6, 0.80%, mp 155-6°C, lit.[13]: 155-6°C had been isolated before from *Tessaria absinthioides*. Its authenticity was confirmed by mmp and direct comparison of the UV, IR and ^{1}H NMR spectra.

The non previously reported ^{13}C NMR agree with the proposed structure (δ 125.93, d, C-1; 199.14, s, C-2; 39.91, t, C-3; 32.84, d, C-4; 40.50, s, C-5; 29.41, t, C-6; 36.24, d, C-7; 29.08, t, C-8; 42.28, t, C-9; 171.28, s, C-10; 144.30, s, C-11; 173.27, s, C-12; 124.93, t, C-13; 19.28, q, C-14; 15.38, q, C-15). Prolonged treatment of the acid 6 with diazomethane afforded the pyrazolinic ester (8) in quantitative yield as an unstable colorless oil. $\nu_{max}^{CHCl_3}$: 1735, 1665 and 1650 cm^{-1}. ^{1}H NMR : δ 5.83 (1H, s, H-1), 4.55 (2H, m, H-16), 3.70 (3H, s, OCH$_3$), 1.05 (3H, s, H-14).

(11S)-11,13-dihydrotessaric acid (7), 0.125%, mp 156-7°C (from acetone-diisopropyl ether), $[\alpha]_D^{20}$ = -190.43° (c 0.209, CHCl$_3$), $C_{15}H_{22}O_3$ (found : C, 72.15; H, 8.99; O, 18.79%; requires : C, 71.97; H, 8.66; O, 19.17%, MS : m/z 250 (M$^+$), 134 (100%)) gave the following UV and IR data : λ_{max}^{MeOH} 238 nm (ε 19836); $\nu_{max}^{CHCl_3}$ 3500, 1745, 1705 cm^{-1}. The ^{1}H NMR spectrum resembles that of tessaric acid (6) except for the signals corresponding to the exomethylene group absent in this molecule. Instead, it showed a doublet at δ 1.15 (J=7 Hz) suggesting that this molecule was a dihydroderivative of 6. The ^{13}C NMR spectrum provides further support to the postulated structure (δ 125.57, d, C-1; 199.12, s, C-2; 38.51, t, C-3; 33.93, d, C-4; 40.22, s, C-5; 28.92, t, C-6; 35.94, d, C-7; 27.48, t, C-8; 42.49, t, C-9; 173.63, s, C-10; 44.37, d, C-11; 180.77, s, C-12; 15.22, q, C-13; 19.35, q, C-14; 14.32, q, C-15). Hydrogenation of 7 in ethyl acetate using Pd/C as catalyst gave the (11S)-tetrahydrotessaric acid (9) as a stereohomogeneous product (90%, mp 128-30°C, $[\alpha]_D^{20}$ = -15.43° (c 0.162, CHCl$_3$), $C_{15}H_{24}O_3$ (MS : m/z 252 (M$^+$), 179 (100%)) showing the following IR and ^{1}H NMR spectral data: $\nu_{max}^{CHCl_3}$ 3450, 1735, 1690 cm^{-1}, δ 8.50 (1H, s, -COOH), 2.75 (1H, m, H-11), 1.22 (3H, d, 7Hz, H-13), 1.10 (3H, s, H-14), 0.85 (3H, d, 7 Hz, H-15) according with the proposed formula 9. Methylation of the acid 7 with ethereal diazomethane gave 10 (95%, colorless oil, $C_{16}H_{24}O_3$ (MS : m/z 264 (M$^+$), 134 (100%)) showing the following spectral data: $\nu_{max}^{CHCl_3}$ 1735, 1665, 1625 cm^{-1}, ^{1}H NMR : δ 5.83 (1H, s, H-1), 3.67 (3H, s, -OC$\underline{H}_3$), 1.10 (3H, d, 7.0 Hz, H-13), 1.03 (3H, s, H-14), 0.85 (3H, d, 7.0 Hz, H-15).

The (11$\underline{S}$)-11,13-dihydrotessaric acid ($\underline{7}$) showed a negative Cotton effect in the CD, opposite to that of nootkatone[14] and similar to the effect showed by tessaric acid and other eremophilanes containing a β oriented C-4 methyl group. The stereochemistry of $\underline{7}$ was unambiguously determined by X-ray analyses.[15] The molecular structure of (11$\underline{S}$)-11,13-dihydrotessaric acid ($\underline{7}$), found in the crystals is shown in the figure.



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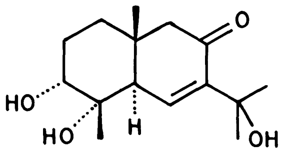

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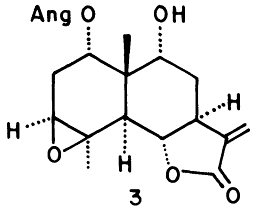

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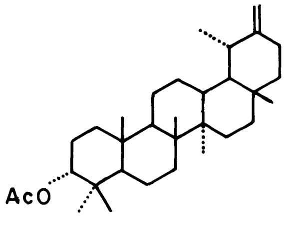

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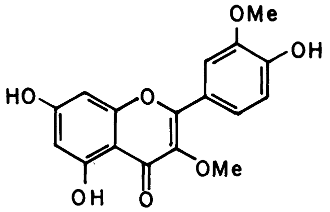

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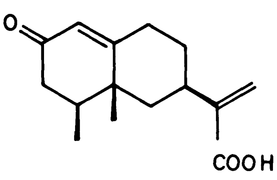

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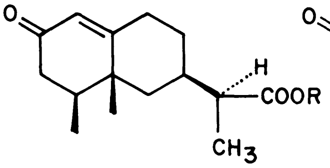
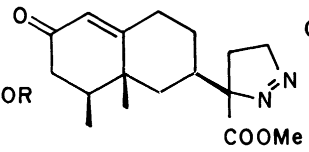


7 R=H
10 R=Me

7



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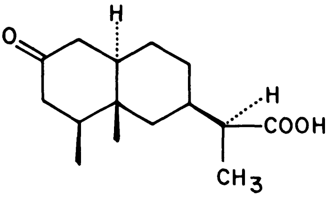

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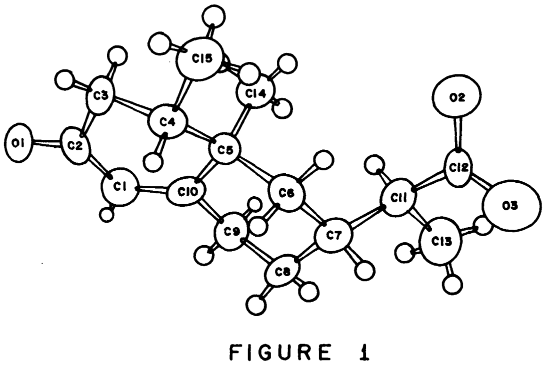

FIGURE 1

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