EtOAc at room temp. was carried out in the usual way, and afforded tetrahydromatricarin, $C_{17}H_{24}O_5$, mp 181–183°, colourless needles, IR ν_{max}^{KBr} cm^{-1}: 1770 (lactone), 1740 (cyclopentanone and acetyl) [7].

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TOMEXANTHIN, AN OXEPANE DITERPENE FROM *MONTANOA TOMENTOSA**

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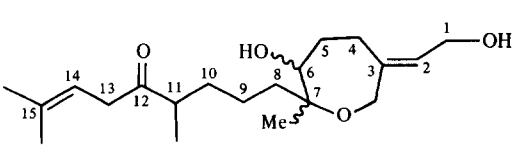
Key Word Index—*Montanoa tomentosa*; Compositae; Heliantheae; oxepane; diterpene.

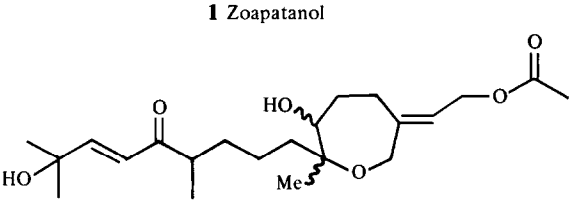
Abstract—Chemical analysis of *Montanoa tomentosa* yielded an oxepane diterpene, tomexanthin, which was characterized by spectral comparison with the previously established zoapatanol.

In continuation of our biochemical systematic analysis of *Montanoa*, the terpenes of *Montanoa tomentosa* Cerv. subsp. *xanthiifolia* (Schultz Bip. in C. Koch) Funk were characterized. In addition to novel sesquiterpene lactones, an oxepane diterpene was isolated which was similar to the known zoapatanol (**1**) a compound of established X-ray structure [1]. Tomexanthin (**2**) differs from **1** by the presence of: (a) an acetyl group at the allylic C-1 position instead of a hydroxyl function, (b) a C-13 double bond instead of one at C-14 and (c) a tertiary hydroxyl group at C-15. The ^1H NMR spectrum of **2** showed the following differences from that of **1**. The two vinyl methyl singlets (δ1.62 and 1.75) of **1** are replaced by a pair of overlapping singlets at δ1.4. A pair of downfield doublets (δ6.38 and 6.92, J = 15.5 Hz) which are characteristic of a *trans*-α,β-unsaturated carbonyl system appear instead of the two signals for H-13 (δ3.12) and H-14 (δ5.47) of **1**. The only other significant difference results from the presence of an acetyl function at C-1 in **2**. Instead of the two-proton doublet (δ4.14) due to H-1a and b of **1** in compound **2** a more downfield absorption at δ4.60 (J = 7 Hz) together with an acetate methyl singlet (δ2.04) appears.

High resolution MS did not yield a molecular ion, but the empirical formula ($C_{22}H_{36}O_6$) was confirmed from the $[M-H_2O]^+$ (378), $[M-C_2H_4O_2]^+$ (336) and $[M-C_2H_4O_2-H_2O]^+$ values. CIMS of **2** confirmed that the molecular weight is 396 ($C_{22}H_{36}O_6$; $[M+1]^+$ = 397). Other significant CIMS peaks occurred at 379 $[M+1-H_2O]^+$, 355 $[M+1-CH_2CO]^+$, 337 $[M+1-AcOH]^+$ and 319 $[M+1-AcOH-H_2O]^+$. Low resolution EIMS produced no molecular ion, but $[M-H_2O]^+$ (378), $[M-CH_2CO]^+$ (354) and $[M-AcOH-H_2O]^+$ (318) characterized the high mass region of the

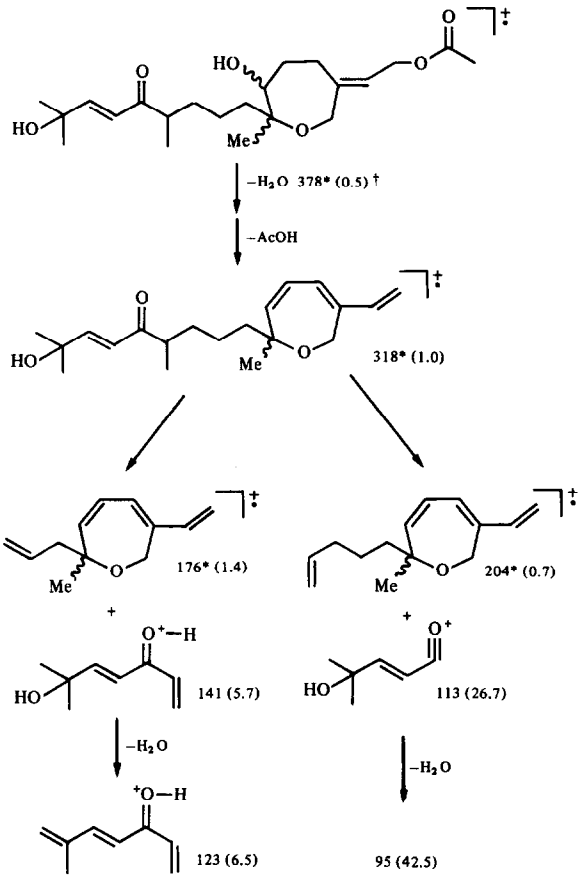


1 Zoapatanol



2 Tomexanthin

*Part 1 in the series "*Montanoa* Terpenes".



Scheme 1. Mass spectral fragmentation pattern of tomexanthin. *Fragments verified by high resolution MS. †Relative intensity.

spectrum and the low mass region included the base peak $[CH_3CO]^+$ (43), $[C_6H_7O]^+$ (95) and $[C_6H_9O_2]^+$ (113).

The EIMS and high resolution MS analyses suggest that following the loss of acetic acid and water there are two competing processes, a McLafferty rearrangement and an allylic cleavage adjacent to the C-12 ketone. Relative intensities indicate that the allylic cleavage is favoured (Scheme 1).

EXPERIMENTAL

For general procedures see ref [2]. NMR spectra were recorded on a Hitachi-Perkin Elmer R600A 60 MHz and a Bruker 200 MHz FT-spectrometers. Mass spectra were obtained on a Hewlett-Packard Model 9585 GC/MS system and high resolution MS data on an AEI MS 902 instrument.

M. tomentosa (FT2813, 35.5 g) was collected near Jacala in the Mexican state of Guerrero on Nov. 12, 1978. The whole dried leaf, stem and head material was extracted twice with CH_2Cl_2 for 2 min and worked up in the usual fashion [2]. The syrup (0.18 g) was chromatographed twice by prep. TLC (silica gel G) using $CHCl_3$–Me_2CO (19:1). Further prep. TLC of band 4 provided the sesquiterpene lactone, 8-acetyl-9-desacylpumilin-9-methacrylate [3], as the major constituent (23 mg). Band 6 of the first prep. TLC run was rechromatographed using the same procedure to yield 11 mg **2**.

Tomexanthin (**2**). $C_{22}H_{36}O_6$, colourless oil; UV λ_{max}^{MeOH} nm: end absorption at 213 (ε 5.3×10^3), 220 (shoulder); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3450 (OH), 1730 (C=O), 1670 (double bond); MS 70 eV *m/z* (rel. int.): 378 (0.5), 354 (1.9), 318 (1.0), 227 (2.3), 210 (11.7), 209 (35.7), 204 (0.8), 176 (1.4), 169 (24.2), 149 (20.8), 141 (5.7), 123 (6.5), 113 (26.7), 95 (42.5), 43 (100.0); CIMS (i-butane, 180°): 397 $[M+1]^+$, 379 $[M+1-H_2O]^+$, 355 $[M+1-CH_2CO]^+$, 337 $[M+1-AcOH]^+$ and 319 $[M+1-AcOH-H_2O]^+$; ^1H NMR (200 MHz, $CDCl_3$, TMS): δ6.92 (H-14, *d*, J = 15.5 Hz), 6.38 (H-13, *d*, J = 15.5 Hz), 5.39 (H-2, *t* (*br*), J = 7 Hz), 4.60 (H-1a and b, *d*, J = 7 Hz), 4.12 [C-3–CH_2–O, *s* (*br*)], 3.54 (H-6, *dd*, J = 4, 8 Hz), 2.75 (H-4a, *dd*), 2.50 (H-4b, *m*), 2.04 (Acetate-Me, *s*), 1.40 [2C-15–Me, *s* (overlapping)], 1.15 (C-7–Me, *s*) and 1.12 (C-11–Me, *d*, J = 7 Hz); [Calc. for $C_{22}H_{34}O_5$ ($M-H_2O$): 378.2405, Found: (MS) 378.2457; Calc. for $C_{20}H_{32}O_4$ ($M-C_2H_4O_2$): 336.2299. Found: (MS) 336.2348; Calc. for $C_{20}H_{30}O_3$ ($M^+-C_2H_4O_2-H_2O$): 318.2194. Found: 318.2193.]

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