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A EUDESMANE ACID FROM *MONTANOA SPECIOSA**

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Key Word Index—*Montanoa speciosa*; Asteraceae; Heliantheae; sesquiterpene; eudesmane.

Abstract—The major constituent of a leaf-surface methylene dichloride wash of *Montanoa speciosa* was a eudesmane acid, 1,2-dehydro-3-oxo-costic acid.

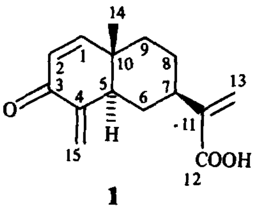
In continuation of our biochemical systematic analysis of *Montanoa* Cerv. (Asteraceae, Heliantheae), the terpenoid constituents of *Montanoa speciosa* DC. were examined. The two major constituents were identified as *ent*-kaurenic acid and a novel eudesmane acid, 1,2-dehydro-3-oxo-costic acid (**1**). The ^{1}H NMR spectrum ($CDCl_3$) of the latter compound differs from that of costic acid (**2**) [1] in, first, the introduction of a pair of sharp doublets at δ6.89 and 6.02 (1 proton each, $J = 10$ Hz) characteristic of an AB pattern of a γ,γ-di-substituted cyclohexenone and, second, the downfield shift of the methylene H-15 proton signals to δ6.11 (overlapping signal, H-15a) and 5.20 (broad singlet, H-15b) from δ4.63 and 4.37, respectively. In C_6D_6–acetone-d_6 (10:1), the H-15a signal of **1** appeared as an unobscured doublet of a doublet ($J = 1.7$, 2.0 Hz). The ^{1}H NMR spectrum ($CDCl_3$) of **1** resembled the spectrum of gerin (**3**) [2] and the related C-6 and C-8 lactonic structures [3, 4]. Comparison of the ^{1}H NMR, IR and UV spectral data of **1** with those reported for **3** indicated that **1** also possessed a ring A cross-conjugated dienone. The UV spectrum of **1** displayed an absorption at 240 nm ($\varepsilon 5.4 \times 10^3$). The IR spectrum showed two strong C=O stretching bands, one at 1688 cm^{-1} associated with the α,β-unsaturated carboxylic acid and the other at 1670 cm^{-1} resulting from a cross-conjugated dienone system. A third strong band at 1614 cm^{-1} (conjugated methylene group) was present. The ^{1}H NMR spectrum ($CDCl_3$) of **1** resembled the spectrum of **3** in all respects except for the absence of the signals associated with the C-12 methoxy and C-8 acetoxy functions of **3**.

The CI-mass spectrum (isobutane) of **1** showed one major peak at m/z 247 $[M + 1]^+$, and the low resolution EI-mass spectrum displayed a prominent peak at m/z 246 $[M]^+$, both consistent with the molecular formula $C_{15}H_{18}O_3$. The difference between this molecular formula and that of **2** ($C_{15}H_{22}O_2$) is consistent with the presence in **1** of an additional double bond and a keto function.

EXPERIMENTAL

For general procedures, see ref. [3]. *Montanoa speciosa* DC. (HF 4202, OS) was collected *ca* 76 miles SW of Oaxaca (Oaxaca, Mexico) on 28 August 1976. The whole dried leaf and stem material (18.5 g) was extracted (× 2) in CH_2Cl_2 for 2 min and worked up in the usual fashion [5], yielding 0.13 g of syrup. Column chromatography of the crude syrup over silica gel (eluant: $CHCl_3$ followed by a $CHCl_3$ and Me_2CO mixture containing an increasing proportion of Me_2CO yielded in fractions 16 and 17 *ent*-kaurenic acid (14 mg) and in fractions 29–32, compound **1** (30 mg).

1,2-Dehydro-3-oxo-costic acid (**1**). Colorless gum, UV λ_{max}^{MeOH} nm (ε): 240 (5.4×10^3), 203 (6.4×10^3); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3060, 2870, 2390, 1700, 1688, 1670, 1613, 1430, 1405, 1365, 1280, 1160, 1105, 1075, 1030, 940, 840; ^{1}H NMR (60 MHz): ($CDCl_3$): δ6.89 (H-1, *d*, $J_{1,2} = 10.0$ Hz), 6.39 (H-13b, *br s*), 6.11 (H-15a, overlapping), 6.02 (H-2, *d*, $J_{1,2} = 10.0$ Hz), 5.75 (H-13a, *br s*), 5.20



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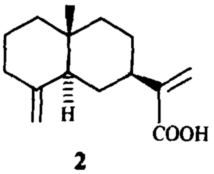

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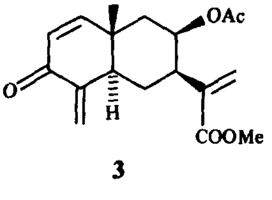

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*Part 6 in the series "*Montanoa* Terpenes".

(H-15b, *br s*), 0.99 (3H-14, *s*); (C_6D_6–Me_2CO-d_6, 10:1): δ6.39 (H-13b), 6.31 (H-1), 6.18 (H-15a, *dd*, $J_{5,15a} = 2.0$, $J_{15a,15b} = 1.7$ Hz), 5.95 (H-2), 5.84 (C12-OH, *br s*), 5.42 (H-13a), 4.91 (H-15b), 0.71 (3H-14); (Me_2CO-d_6): δ6.91 (H-1), 6.17 (H-13b), 5.92 (H-15a), 5.87 (H-2), 5.70 (H-13a), 5.16 (H-15b), 1.00 (3H-14); MS *m/z* (rel. int.): 247.9 (6), 247.0 (18), 246.0 $[M]^+$, $C_{15}H_{18}O_3$ (19), 230.9 $[M - Me]^+$ (10), 228 $[M - H_2O]^+$ (11), 213.0 (6), 200.9 (11), 199.9 (8), 173.0 (9), 159.0 (9), 135.1 (13), 91.0 (25), 43.1 (20), 41.0 (21), 31.9 (33), 28 (100); CIMS (isobutane) *m/z* (rel. int.): 247.1 $[M + 1]^+$ (100), 229 $[M + 1 - H_2O]^+$ (8).

REFERENCES

1. Bawdekar, A. S. and Kelkar, G. R. (1965) *Tetrahedron* **21**, 1521.
2. Rodriguez, E., Sanchez, B., Grieco, P. A., Majetich, G. and Oguri, T. (1979) *Phytochemistry* **18**, 1741.
3. Bohlmann, F. and Zdero, C. (1982) *Phytochemistry* **21**, 647.
4. Geissman, T. A. and Mukherjee, R. (1968) *J. Org. Chem.* **33**, 656.
5. Yoshioka, H., Mabry, T. J. and Timmermann, B. N. (1973) *Sesquiterpene Lactones*. University of Tokyo Press, Tokyo.

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CLERODANE DITERPENOIDS FROM *ASTER ALPINUS*

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Key Word Index—*Aster alpinus*; Compositae; diterpenes; clerodane derivatives.

Abstract—The aerial parts of *Aster alpinus* afforded, in addition to dammadienyl acetate and dammadienone, two clerodane derivatives related to salviarin and bacchotricuneatin A. The structures were elucidated by spectroscopic methods, especially high-field NMR. The chemotaxonomic situation is discussed briefly.

INTRODUCTION

From the large genus *Aster* (Compositae, tribe Astereae) several species have already been studied. In addition to acetylenic compounds [1, 2], umbelliferone derivatives of sesquiterpenes may be characteristic of some groups [3]. So far, only one species has given sesquiterpene lactones [4]. We have now studied *Aster alpinus* L. Only some unusual fatty acids [5] and, from the roots, lachnophyllum ester [1] were reported from this species. The results are discussed in this paper.

RESULTS AND DISCUSSION

The aerial parts of the widespread perennial *Aster alpinus* L., collected in the Mongolian Peoples Republic, afforded dammadienyl acetate and dammadienone as well as two diterpenes, the clerodane derivatives **1** and **2**.

The molecular formula of **1** was $C_{25}H_{28}O_8$ and the loss of 99 mu and a strong fragment at *m/z* 83 ($C_4H_7CO^+$) indicated the presence of an unsaturated C_5-ester. The ^1H NMR spectrum (Table 1) showed that this ester group was an angelate as followed from the typical signals (δ6.16 *qq*, 2.03 *dq* and 1.85 *dq*). Furthermore, characteristic signals of a β-substituted furan could be recognized. A pair of doublets at δ3.85 and 4.66 indicated an oxygen-bearing methylene group, most likely part of a γ-lactone, its presence also being indicated by the IR spectrum. A slightly broadened double-doublet at δ5.30 was coupled with one of the furan protons. Accordingly, this signal could be assigned to H-12, which must be located at an oxygen-bearing carbon. Spin decoupling, especially in deuteriobenzene, allowed the assignment of all signals. The sequences obtained were interrupted by two quaternary carbons and by carbonyl groups. However, a W-coupling between H-19α and H-6 indicated the connection between the two sequences and showed that C-5 was quaternary. As the singlet at δ2.63 showed a weak W-coupling with H-20 and only H-8 was coupled with H-7, the remaining groups had to be placed in a clerodane skeleton. The stereochemistry was supported by a W-coupling between H-2β and H-4, by the magnitude of the couplings of H-6, H-8 and H-12, and by NOE difference spectroscopy. Irradiation of H-20 caused clear NOEs with H-11β (7%), H-8 (6%), H-19α (6%), H-19β (3%) and H-12 (1.5%). Furthermore, NOEs between H-8 and H-12 (10%) and between H-4 and H-6 (10%) were observed. Inspection of models showed that this could be expected only if ring C was in a boat form, obviously due to the β-substituent at C-12 which would be axial in a chair form. The small coupling of H-4 also required a boat conformation for ring A. This is possibly due to some steric hindrance between C-18 and the angelate residue which