

SHORT COMMUNICATION

SESQUITERPENE LACTONES OF *HYMENOCLEA MONOGYRA*¹

F. P. TORIBIO and T. A. GEISSMAN

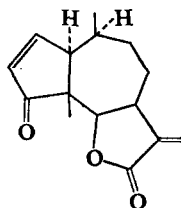
Department of Chemistry, University of California, Los Angeles, California 90024

(Received 19 August 1968)

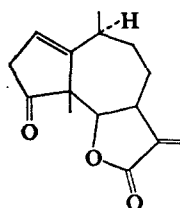
Abstract—Ambrosin, neoambrosin, psilostachyin, psilostachyin C, ilicic acid and costunolide have been identified in *Hymenoclea monogyra*.

A RECENT study² of *Hymenoclea salsola* T. and G. showed that this plant, a member of the tribe Ambrosieae of the family Compositae, has a chemical constitution closely resembling those of several *Ambrosia* species. This study has now been extended to *H. monogyra* T. and G., a species common to Arizona.

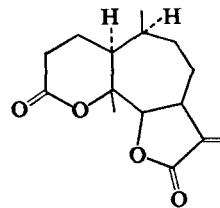
Six sesquiterpenes, all known in other composites and most of them characteristic of members of the Ambrosieae, have been isolated from this plant. Ambrosin (I), neoambrosin (II), psilostachyin (III), psilostachyin C (IV), and ilicic acid (V) have all been found in numerous species of *Ambrosia* and in *H. salsola*. The sixth constituent of *H. monogyra* is costunolide (VI), a well-known sesquiterpene lactone but not heretofore encountered in plants of this tribe. The presence of costunolide along with ilicic acid is of incidental interest, for costunolide represents the sesquiterpene lactone closest to the hypothetical cyclodecadiene



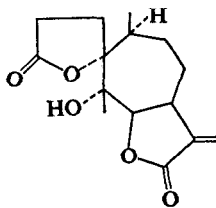
Ambrosin (I)



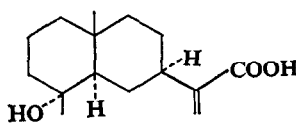
Neoambrosin (II)



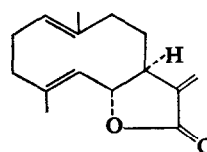
Psilostachyin (III)



Psilostachyin c (IV)



Ilicic Acid (V)



Costunolide (VI)

¹ Contribution No. 2282 from the Department of Chemistry, U.C.L.A.

² T. A. GEISSMAN and F. P. TORIBIO, *Phytochem.* 6, 1563 (1967).

from which these compounds are probably derived. The co-occurrence of costunolide, the eudesmane-derived ilicic acid, the two pseudoguaianolides I and II, and the pseudoguaianolide-derived dilactones III and IV presents a provocative picture of a structurally closely related group of compounds, and one that provides additional reinforcement to the hypothesis that these compounds are intimately allied in their biosynthetic origins.

EXPERIMENTAL

Three kg of *Hymenoclea monogyra* (Voucher No. RJB-766-NM), collected in June 1966, near Tucson, Arizona,³ was extracted with CH_2Cl_2 at room temperature and the extract processed as described previously.² The final mixture of the crude constituents was dissolved in CHCl_3 and extracted with 5% NaHCO_3 . From the aqueous extract was recovered 3.6 g (0.12 per cent) of *ilicic acid* (V), identified by direct comparison (m.p., i.r., NMR and TLC) with an authentic specimen.

The neutral materials remaining after the carbonate extraction were recovered by removing the CHCl_3 and the resulting oily mixture was chromatographed on silica gel with successive elution with benzene, CHCl_3 , CHCl_3 -ethyl acetate, and CHCl_3 -ethyl acetate-acetone. Eluted fractions were examined by TLC, and those showing the same components were combined and evaporated under reduced pressure. The following compounds were obtained:

Costunolide (VI),^{4,5} $\text{C}_{15}\text{H}_{20}\text{O}_4$, m.p. 108–110° (reported,⁴ 106–107°). It was identified by direct comparison with an authentic specimen.⁵ The yield was 0.01 per cent. *Neoambrosin* (II),^{2,6} $\text{C}_{15}\text{H}_{18}\text{O}_3$, m.p. 126–127°, was identified by direct comparison with a sample isolated from *H. salsola*.² Yield, 0.03 per cent. *Ambrosin* (I),^{7,8} $\text{C}_{15}\text{H}_{18}\text{O}_3$, m.p. 148–150° was identified by comparison with a specimen isolated from *H. salsola*. Yield, 0.02 per cent. *Psilostachyin* (III),⁹ $\text{C}_{15}\text{H}_{20}\text{O}_5$, m.p. 218–220°, was identified by comparison with an authentic specimen. Yield, 0.025 per cent. *Psilostachyin C* (IV),¹⁰ $\text{C}_{15}\text{H}_{20}\text{O}_4$, m.p. 228–230° reported,¹⁰ m.p. 223–225°, was identified by comparison with an authentic specimen. Yield, 0.05 per cent.

Acknowledgements—This study was carried out with the aid of a research grant, GM-14240-01, from the U.S. Public Health Service. Elemental analyses are by Miss Heather King.

³ We are grateful to Mr. R. J. Barr, Tucson, Arizona, for collecting the plant and establishing its identity.

⁴ A. S. RAO, G. R. KELKAR and S. C. BHATTACHARYA, *Chem. & Ind.* 1359 (1958).

⁵ We are indebted to Dr. B. Tilak, National Chemical Laboratory, Poona, India, for a specimen of costunolide.

⁶ A. ROMO DE VIVAR, L. RODRIGUEZ-HAHN, J. ROMO, M. V. LAKSHMIKANTHAM, R. N. MIRRINGTON, J. KAGAN and W. HERZ, *Tetrahedron* **22**, 3279 (1966).

⁷ W. HERZ, W. WATANABE, M. MIYAZAKI and Y. KISHIDA, *J. Am. Chem. Soc.* **84**, 2601 (1962).

⁸ W. HERZ and Y. SUMI, *J. Org. Chem.* **29**, 3438 (1964).

⁹ H. E. MILLER, H. B. KAGAN, W. RENOLD and T. J. MABRY, *Tetrahedron Letters* 3397 (1965).

¹⁰ H. B. KAGAN, H. E. MILLER, W. RENOLD, M. V. LAKSHMIKANTHAM, L. R. TETHER, W. HERZ and T. J. MABRY, *J. Org. Chem.* **31**, 1629 (1966).