EM reagents) with Skelly F–Et_2O–C_6H_6 (6:3:1) as eluent and further separated by repeated prep. TLC (Si gel, E. Merck). The herb sample afforded 125 mg **1**, 9 mg **3**, 5 mg **5** and 7 mg **6**. GC was carried out on a Hewlett–Packard 5830A chromatograph with a 18 m 30% SE-30 capillary column at 160° with N_2 flow rate of 30 ml/min.

Tetrahydroligularenolide (**3**). Isolated as colourless crystals; mp 91–92°; EIMS (probe) 70 eV, m/z (rel. int.): 234 $[M]^+$ (23), 125 $[M-109]^+$ (45), 123 $[M-111]^+$ (100), 112 $[M-122]^+$ (42), 110 $[M-124]^+$ (39); IR ν_{max} (film) cm^{-1}: 1735 (C=O), 1685 (C=C); ^1H NMR (200 MHz): δ 0.58 (3H, *s*, H-14), 0.90 (3H, *d*, $J_{15,4} = 5.7$ Hz, H-15), 1.78 (3H, *m*, H-13), 2.76(1H, *d*, $J_{6\beta,6\alpha} = 14.0$ Hz, H-6β), 4.62(1H, *m*, H-8). This material cochromatographed (GC) with a synthetic sample of **3** (R_t 1.00) and displayed a R_t different from eremophilenolide (**2**) (R_t 1.01). The above spectroscopic data was found to match values obtained with the synthetic sample of **3** and lit. values [6, 7, 11].

Acknowledgements—We wish to thank Dr. L. T. Gelbaum of the Georgia Institute of Technology, Atlanta, Georgia for an authentic sample of *trans*-9-oxofuranoeremophilane and Dr. E. Piers at the University of British Columbia, Vancouver, Canada for providing samples of synthetic tetrahydroligularenolide and eremophilenolide.

REFERENCES

1. Krochmal, A., Walters, R. S. and Doughty, R. M. (1971) *A Guide to Medicinal Plants of Appalachia*. Agricultural Handbook No. 400, U.S. Department of Agriculture.
2. Lewis, W. H. and Elvin-Lewis, M. P. F. (1977) *Medical Botany* p. 322. John Wiley, New York.
3. Bohlmann, F., Knoll, K-H., Zdero, C., Mahanta, P-K., Grenz, M., Suwita, A., Ehlers, D., Van, N-L., Abraham, W-R. and Natu, A-N. (1977) *Phytochemistry* **16**, 965.
4. Zalkow, L. H., Gelbaum, L. T. and Derveer, D. V. (1979) *J. Chem. Soc. Perkin Trans.* 1, 1542.
5. Jennings, P. W. (1978) in *Effects of Poisonous Plants on Livestock* (Keeler, R. F., Van Kampen, K. R. and James, L. F., eds.) p. 217. Academic Press, New York.
6. Tanahashi, Y., Ishizaki, Y., Takahashi, T. and Tori, K. (1968) *Tetrahedron Letters* 3739.
7. Ishizaki, Y., Tanahashi, Y., Takahashi, T. and Tori, K. (1970) *Tetrahedron* **26**, 5387.
8. Hayashi, K., Nakamura, H. and Mitsuhashi, H. (1973) *Phytochemistry* **12**, 2931.
9. Naya, K., Tsuji, K. and Haku, U. (1972) *Chem. Letters* 235.
10. Bohlmann, F., Kramp, W., Robinson, H. and King, R. M. (1981) *Phytochemistry* **20**, 1739.
11. Yamakawa, K., Kobayashi, M., Hinata, S. and Satoh, Y. (1980) *Chem. Pharm. Bull.* **28**, 3265.

Phytochemistry, Vol. 22, No. 3, pp. 782–783, 1983.
Printed in Great Britain.

0031-9422/83/030782-02$03.00/0

A SESQUITERPENOID LACTONE FROM *AMBROSIA CUMANENSIS**

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(*Revised received* 28 *June* 1982)

Key Word Index—*Ambrosia cumanensis*; Heliantheae; Compositae; bark; sesquiterpenoid lactone; psilostachyinolides; 10α-hydroxyisopsilostachyin C; coniferaldehyde; syringaldehyde.

Abstract—A new psilostachyinolide, 10α-hydroxyisopsilostachyin C, and the phenols coniferaldehyde and syringaldehyde have been isolated from the bark of *Ambrosia cumanensis*.

INTRODUCTION

Continuing our studies of the family Compositae from El Salvador [1, 2], especially the aerial parts of *Ambrosia cumanensis* [3–5], we now report the isolation and structure of a major compound isolated from the bark of this species. The aim of this work was to explore possible relationships between the components of the bark and the sesquiterpenoid lactones obtained from the aerial parts. In previous work [3–5] we reported seven psilostachyinolides from the aerial parts of *A. cumanensis*. These sesquiterpenoid lactones show remarkable differences according to the geographical location of the botanic samples [6]. Ambrosanolides and psilostachyinolides are isolated as the major components.

RESULTS AND DISCUSSION

Compound **1**, $C_{15}H_{20}O_5$, was obtained from a petrol extract of the bark of *A. cumanensis* as a viscous oil. The

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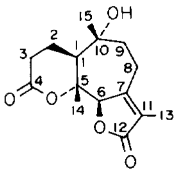
*Part 4 in the series 'Salvadorian Compositae'. For Part 3 see, Arriaga-Giner, F. J., Borges-del-Castillo, J., Manresa-Ferrero, M. T., Peña-Recinos, S. and Rodríguez-Luis, F. *Rev. Latinoam. Quim.* (*in press*).



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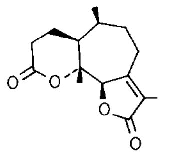

2

IR spectrum showed bands at 3485 (OH), 1755 and 1720 (C=O) and 1640 cm^{-1} (C=C). The UV spectrum exhibited a maximum at 225 nm. The MW determined by mass spectrometry was 280.127 (for $C_{15}H_{20}O_5$). The ^1H NMR spectrum revealed absorbances at δ 4.70 (corresponding to the lactone closing α-proton, H-6), three methyl groups at 1.72 (*br s*, Me-13), 1.05 (*s*, Me-14) and 1.23 (*s*, Me-15). In addition there was a signal at δ 1.55 that disappeared with D_2O. The ^1H NMR spectrum of **1** was very similar to that of isopsilostachyin C **2** [3–5], with the exception of the methyl group at C-10, which appeared in **1** as a singlet as indicated above. The stereochemistry of C-10 was established on the basis of biogenetic considerations and comparison with similar compounds [6]. The structure of **1** is, therefore, concluded to be 10α-hydroxyisopsilostachyin C. This compound had been detected earlier in the aerial parts of this species, together with the other psilostachyinolides, but because of the very small amounts present we could not establish its structure previously.

The chloroform extract afforded two phenolic compounds. The first one, mp 84° showed a ^1H NMR spectrum (see Experimental) which conformed with the structure of 4-hydroxy-3-methoxycinnamaldehyde (coniferaldehyde). The other compound, mp 111°, showed a ^1H NMR spectrum identifying it as 4-hydroxy-3,5-dimethoxybenzaldehyde (syringaldehyde). The physical constants of both compounds were consistent with those reported in the literature [7, 8].

EXPERIMENTAL

Ambrosia cumanensis was collected in July 1979, in the neighbourhood of the El Salvador University, Republic of El Salvador. The dried plant bark (7.9 kg) was extracted with EtOH (80 l.) for 70 hr under reflux. The extract (61.29 g) was filtered, concd to 1 l. and diluted with an equal vol. of H_2O. This soln was extracted successively with petrol and $CHCl_3$.

The petrol extract was steam distilled, yielding an oil (3 g) which was chromatographed on Si gel, eluted first with C_6H_6, and then with C_6H_6 containing increasing proportions of EtOAc. Elution with C_6H_6–EtOAc (9:1) yielded 38 mg 10α-hydroxyisopsilostachyin C (**1**) and C_6H_6–EtOAc (8:2) gave 12 mg of an unidentified compound, $C_{14}H_{30}N_4O_2$.

10α-Hydroxyisopsilostachyin C (**1**). $[\alpha]_D^{20}$ −0.47° ($CHCl_3$; *c* 0.4); IR ν_{max}^{Nujol} cm^{-1}: 3485 (OH), 1755 (C=O), 1720 (C=O), 1640 (C=C); UV λ_{max}^{EtOH} nm: 225; ^1H NMR ($CDCl_3$): see Results and Discussion; MS *m/z* (rel. int.): 280.127 (for $C_{15}H_{20}O_5$), 238 $[M-C_2H_2O]^+$ (10), 252 $[M-CO]^+$ (1), 153 (100), 149 (65), 137 (56), 135 (68), 81 (36).

The $CHCl_3$ extract (29.21 g) was chromatographed on Si gel and the column was eluted first with C_6H_6 and then with C_6H_6–EtOAc mixtures. C_6H_6–EtOAc (9:1) yielded 31 mg coniferaldehyde and C_6H_6–EtOAc (8:2) gave 48 mg syringaldehyde.

Coniferaldehyde. Mp 84° (C_6H_6–petrol); IR ν_{max}^{Nujol} cm^{-1}: 3450 (OH), 2760 (CHO), 1690 (C=O), 1640 (C=C), 980 (C=C); UV λ_{max}^{EtOH} nm: 270, 262, 256, 250; ^1H NMR ($CDCl_3$): δ 3.86 (3H, *s*, –OMe), 6.39 (1H, *dd*, $J_{\alpha,\beta} = 16$ Hz, $J_{\beta,\gamma} = 7$ Hz) and 6.65 (1H, *dd*, $J_{\alpha,\beta} = 16$ Hz, $J_{\alpha,\gamma} = 7$ Hz), (α- and β-protons of the side chain), 6.70 (1H, *br*, *s*, disappears with D_2O, OH-4), 6.80 (1H, *d*, $J_{5,6} = 8.5$ Hz, H-5), 6.93 (1H, *d*, $J_{2,6} = 1.5$ Hz, H-2), 7.50 (1H, *dd*, $J_{5,6} = 8.5$, $J_{2,6} = 1.5$ Hz, H-6), 9.10 (1H, *d*, $J_{\beta,\gamma} = 7$ Hz, aldehydic proton); MS, *m/z* (rel. int.): 178.56 (for $C_{10}H_{10}O_3$, 100), 163 (10), 149 (40), 135 (35), 109 (25), 79 (15), 77 (25), 71 (15).

Syringaldehyde, Mp 111° (petrol); IR ν_{max}^{Nujol} cm^{-1}: 3100 (OH), 1685 (C=O); UV λ_{max}^{EtOH} nm: 280, 233, 228, 220, 204; ^1H NMR ($CDCl_3$): δ 3.90 (6H, *s*, OMe), 6.55 (1H, *br s*, disappears with D_2O, OH-4), 7.10 (2H, *s*, H-2 and H-6), 9.80 (1H, *s*, aldehydic proton); MS, *m/z* (rel. int.): 182.105 (for $C_9H_{10}O_4$, 100), 167 (17), 153 (10), 149 (27), 111 (12), 79 (7).

Acknowledgements—We are grateful to Professor C. J. W. Brooks for mass spectra. Financial support was provided by the Comisión Asesora de Investigación Científica (Spain).

REFERENCES

1. Borges-del-Castillo, J., Manresa-Ferrero, M. T., Rodríguez-Luis, F., Vázquez-Bueno, P., Genovés-Leonor, N. and Portillo de Rivas, R. M. (1981) *An. Quim.* **77**, 90.
2. Borges-del-Castillo, J., Manresa-Ferrero, M. T., Rodríguez-Luis, F., Vázquez-Bueno, P., Genovés-Leonor, N. and Castillo-Arévalo, S. (1981) *J. Nat. Prod.* **44**, 348.
3. Borges-del-Castillo, J., Manresa-Ferrero, M. T., Martín-Ramón, J. L., Pascual-Rigau, C. and Vázquez-Bueno, P. (1978) *Tetrahedron Letters* 1513.
4. Borges-del-Castillo, J., Manresa-Ferrero, M. T., Martín-Ramón, J. L., Rodríguez-Luis, F. and Vázquez Bueno, P. (1980) *An. Quim.* **76**, 277.
5. Borges-del-Castillo, J., Manresa-Ferrero, M. T., Martín-Ramón, J. L., Rodríguez-Luis, F. and Vázquez Bueno, P. (1981) *An. Quim.* **77**, 52.
6. Yoshioka, H., Mabry, T. J. and Timmerman, B. N. (1973) *Sesquiterpene Lactones.* University of Tokyo Press, Tokyo.
7. Greighton, R. H. J., Gibbs, R. D. and Hibbert, H. (1944) *J. Am. Chem. Soc.* **66**, 32.
8. Black, R. A., Rosen, A. and Adams, S. L. (1953) *J. Am. Chem. Soc.* **75**, 5344.