

the general chromatography (1.2 g; petrol-Et₂O, 19:1; 0.41), mainly consisting of tirucallol (**2d**), were collected and recrystallized several times from MeOH. Chromatography of the mother liquors on 3% AgNO₃/Si gel (petrol-Et₂O, 19:1) afforded more tirucallol besides a small amount (150 mg) of crude **1e**, which after further purification was an oil [α]_D²⁰ + 3° (c = 0.8). (Found: C, 84.61; H, 11.94. C₃₀H₅₀O requires: C, 84.44; H, 11.81%; MW 426 (MS); IR ν_{max} cm⁻¹: 3400; ¹H NMR: δ 5.20 (*br m*, 2H). A pure sample of **1e** was compared and found identical with a semi-synthetic sample specially prepared (see above) from methyl masticadienonate (**1a**).

Acknowledgements—This work was supported by the Italian National Research Council (CNR). The authors are gratefully indebted to Dr. D. Wool, Tel Aviv University, for generously providing the starting material and for his helpful advice and discussions.

REFERENCES

1. Caputo, R. and Mangoni, L. (1970) *Gazz. Chim. Ital.* **100**, 317.
2. Monaco, P., Caputo, R., Palumbo, G. and Mangoni, L. (1973) *Phytochemistry* **12**, 939.
3. Barton, D. H. R. and Seoane, E. (1956) *J. Chem. Soc.* 4150.
4. Seoane, E. (1956) *J. Chem. Soc.* 4158.
5. Cheung, H. T. and Feng, M. C. (1968) *J. Chem. Soc.* 4150.
6. Caputo, R., Mangoni, L., Monaco, P., Palumbo, G., Aynehchi, Y. and Bagheri, M. (1978) *Phytochemistry* **17**, 815.
7. Arigoni, D., Jeger, O. and Ruzicka, R. (1955) *Helv. Chim. Acta* **38**, 222.
8. Crabbé, P., Ourisson, G. and Takahashi, T. (1958) *Tetrahedron* **3**, 279.
9. Shamma, M. and Rosenstock, P. D. (1959) *J. Org. Chem.* **24**, 726.
10. Mills, J. S. (1956) *J. Chem. Soc.* 2196.
11. Monaco, P., Caputo, R., Palumbo, G. and Mangoni, L. (1973) *Phytochemistry* **12**, 2534.
12. Simonsen, G. and Ross, L. (1951) *The Terpenes*, Vol. 4, Cambridge University Press, London.
13. Monaco, P., Caputo, R., Palumbo, G. and Mangoni, L. (1974) *Phytochemistry* **13**, 1972.
14. Dauben, H. J., Löken, B. and Ringol, H. J. (1954) *J. Am. Chem. Soc.* **76**, 1359.
15. Loewenthal, H. J. E. (1959) *Tetrahedron* **6**, 269.
16. Karrer, P. and Saemann, R. (1952) *Helv. Chim. Acta* **35**, 1932.

Phytochemistry, 1979, Vol. 18, pp. 898–899. © Pergamon Press Ltd. Printed in England.

0031-9422/79/0501-0898 \$02.00/0

TRITERPENE QUINONE-METHIDES FROM *SCHAEFFERIA CUNEIFOLIA* ROOTS*

X. A. DOMÍNGUEZ, R. FRANCO, G. CANO, S. GARCÍA, A. ZAMUDIO, B. AMEZCUA

and X. A. DOMÍNGUEZ, JR.

Department of Chemistry, I.T.E.S.M., Sucursal de Correos 'J', Monterrey, N.L., Mexico

(Received 11 September 1978)

Key Word Index—*Schaefferia cuneifolia*; Celastraceae; sitosterol; epifriedelanol; pristimerin; tingenone; germination inhibitors; dulcitol.

Abstract—The two quinone-methides, pristimerin and tingenone, have been isolated from the roots of *Schaefferia cuneifolia*. Both compounds strongly inhibit the germination of lentil seeds.

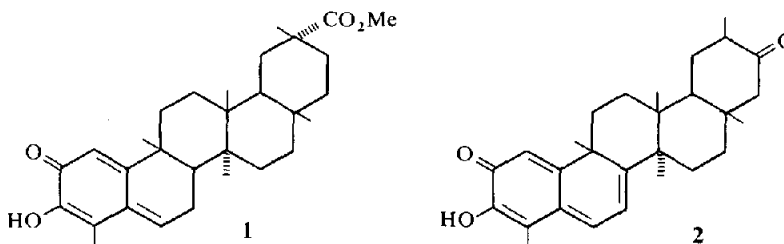
The Celastraceae is a relatively small, widely distributed family, several species of which are used in folk medicine [1]. From *Maytenus* sp. and *Tripterygium wilfordii*, highly active tumor inhibitory alkaloids have been isolated [2, 3]. There are 33 Mexican native species from this family and 8 of them are used for medicinal purposes [4]. In particular, the reddish roots of *Schaefferia cuneifolia* A. Gray (capul), are used as a remedy for venereal diseases. We have found that the root extracts from this plant contain sitosterol, epifriedelanol, pristimerin **1** and

tingenone **2**. On a bioassay of **1** and **2** with corn and lentil seeds, both triterpene quinone-methides exhibited strong inhibitory activity toward the germination of lentil seeds [5].

EXPERIMENTAL

The mps are uncorr. The elemental analyses were obtained in Alfred Bernhardt Laboratories, Engelskirchen, Germany. For TLC and column chromatography, Si gel (Merck) was used. Air-dried roots (950 g) of *Schaefferia cuneifolia* (collected at Grutas de García, N.L., in June 1975, a voucher specimen XAD 7489, is deposited in the Herbarium, I.T.E.S.M.), were ground

* Part 33 in the series "Mexican Medicinal Plants". For Part 32 see (1978) *Rev. Latinoam. Quím.* **9**, 33.



to a fine powder which was successively extracted in a Soxhlet with petrol and ethanol. On preliminary chemical screening of each extract [6], no alkaloid or flavonoids could be detected. The reddish petrol extract (16 g) was refluxed 1 hr with 160 ml MeOH and the suspension was filtered. The methanolic filtrate was evapd and 3 g of the residue were chromatographed on a Si gel column, affording sitosterol (195 mg), epifriedelanol, epifriedelanyl acetate, pristimerin and tingenone. All five compounds were identified by direct comparison with authentic specimens. From the ethanolic extract only dulcitol (1.8 g) was isolated and its identity was ascertained by IR, NMR, mmp and co-TLC, and from the properties of its hexacetate.

Acknowledgements—To the World Health Organization for a research grant No. 77051 and to Syntex de Mexico for financial help. We wish to thank Prof. Dr. G. B. Marini-Bettolo, from Italy and A. González González from Spain, for supplying us

with authentic samples of celastrol, pristimerin and tingenone, and Ing. H. Gómez Junco and Dr. J. Treviño Abrego for MS.

REFERENCES

1. Marini-Bettolo, G. B. (1974) *Il. Farmaco, Ed. Sci.* **29**, 550.
2. Kupchan, S. M. and Smith, R. M. (1977) *J. Org. Chem.* **42**, 115.
3. Kupchan, S. M., Hintz, H. P. J., Smith, R. M., Karim, A., Cass, N. W., Court, W. A. and Yatagai, M. (1977) *J. Org. Chem.* **42**, 3660.
4. Domínguez, X. A., Franco, R., Cano, G., García, S. and Peña, V. (1978) *Rev. Latinoam. Quím* **9**, 33.
5. Domínguez, X. A., Rovalo, M., Rojas, G. M. and Espinosa, G., unpublished results.
6. Domínguez, X. A. (1973) *Métodos de Investigación Fitoquímica*. Limusa-Wiley, México.

A NEW STEROL, 4 α -METHYL-5 α -ERGOSTA-8(14),24(28)-DIEN-3 β -OL, FROM THE MARINE DINOFLAGELLATE *AMPHIDINIUM CARTERAE*

NANCY W. WITHERS, L. JOHN GOAD and TREVOR W. GOODWIN

Department of Biochemistry, University of Liverpool, P.O. Box 147, Liverpool, L69 3BX, U.K.

(Received 26 October 1978)

Key Word Index—*Amphidinium carterae*; *Amphidinium* species; dinoflagellates; algae; sterols; amphisterol; 4 α -methyl-5 α -ergosta-8(14),24(28)-dien-3 β -ol; cholesterol.

Many novel sterols have been isolated from marine invertebrate organisms [1–4] and it is considered that at least some of these may be derived in the animals diet from algal sources. In the quest for the algae responsible for the biosynthesis of unusual sterols, attention has recently been focused upon dinoflagellate species. Shimizu *et al.* [5] reported the isolation of an unusual 4 α -methylsterol, dinosterol (1) and cholesterol from the photosynthetic dinoflagellate *Gonyaulax tamarensis*. In an examination of the non-photosynthetic organism *Crypthecodinium cohnii*, we [6] also found dinosterol (1)

as the major sterol but in addition identified the corresponding Δ^5 compound, dehydrosinosterol (2), the 3-oxo derivative (3) and a small amount of cholesta-5,7-dien-3 β -ol. We have also reported studies on the mechanism of methylation of the dinosterol (1) side chain [7]. In our continuing studies of the dinoflagellate sterols, we now report the characterization of another new sterol, 4 α -methyl-5 α -ergosta-8(14),24(28)-dien-3 β -ol (4), for which we suggest the trivial name amphisterol, from *Amphidinium carterae* and other *Amphidinium* species.

Amphidinium carterae (Py-1) was grown [8] at 18°,