

## TERPENES, COUMARINS, AND FLAVONES

### FROM *Acacia pennatula*

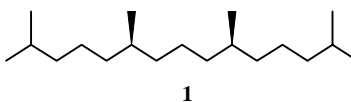
M. Y. Rios

UDC 547.972

The chemical analysis of the acetone extract of the dried leaves from *Acacia pennatula* yielded triacontanol,  $\beta$ -sitosterol palmitate,  $\beta$ -sitosterol, squalene, nonaprenol, norphytane, lupenone, lupeol, daphnetin and catechin, while from the methanol extract were isolated catechin, epigallocatechin, eriodictyol,  $\beta$ -sitosteryl- $\beta$ -D-glucopyranoside, and stigmasteryl- $\beta$ -D-glucopyranoside. The structures of all these natural products were established based on their IR,  $^1\text{H}$ , and  $^{13}\text{C}$  NMR and MS data.

**Key words:** *Acacia pennatula*, Leguminosae, terpenes, coumarins, flavones.

Several chemical studies have been performed on species of the *Leguminosae* family, one of the biggest and most important families of the vegetable kingdom [1]. *Acacia* is a genus belonging to this family and includes approximately 1.200 species. Of these, 64 species are located in Mexico, where some of them are used in the folkloric medicine for the treatment of cancer, gastrointestinal ailments, respiratory infections, diabetes, headache and paludism. A decoction from the aerial parts of *A. pennatula* (common name "algarrobo") is employed at Morelos, as a traditional medicine for the treatment of inflammation and cancer [2]. *A. pennatula* (Cham. & Schltdl.) Benth. is a shrub or tree growing up to 3 m high, found throughout the southern states of Mexico, and to our knowledge, no phytochemical investigation has been carried out on this species so far. In this analysis, from the dried leaves fourteen natural products were isolated: triacontanol [3],  $\beta$ -sitosterol palmitate [4],  $\beta$ -sitosterol, squalene [5], nonaprenol [6], meso-2,6,10,14-tetramethylpentadecane (norphytane, **1**) [7], lupenone [8], lupeol [9], daphnetin [10], catechin [11], epigallocatechin [11], eriodictyol [12], 3-O- $\beta$ -D-glucopyranosyl- $\beta$ -sitosterol (daucasterol) [13], and stigmasteryl- $\beta$ -D-glucopyranoside [14]. Compound **1** has been obtained from shark liver oil, herring oil, wool wax and zooplankton [15]; however, this is the first occasion that this natural product is isolated from a plant. The sterols, lupane triterpenes, and flavan-3-ols are compounds previously isolated from *Acacia* species [16], establishing that this species is chemically similar to other species of *Acacia* genus.



## EXPERIMENTAL

**General Experimental Procedures.** The acetone and methanol extracts from *A. pennatula* were fractioned by means of open CC (Merck Kiesel-gel 60 and Supelclean<sup>TM</sup> SPE LC-SI 6 mL Tubes), and TLC (ALUGRAM<sup>®</sup> SIL G/UV<sub>254</sub> silicagel plates), using mixtures of *n*-hexane–acetone as eluent. In the TLC analysis, the compounds were visualized by UV light and spraying with a 1% solution of  $(\text{NH}_4)_4\text{Ce}(\text{SO}_4)_2$  in 2N  $\text{H}_2\text{SO}_4$ ; IR spectra were recorded with a Bruker Vector 22 IR instrument in  $\text{CHCl}_3$  solution;  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded in  $\text{CDCl}_3$  on a Varian Unity 400 and Varian-Gemini 200 spectrometers, and the chemical shifts were expressed in parts per million ( $\delta$ ) relative to TMS as internal standard. Mass spectra

---

Centro de Investigaciones Químicas de la Universidad Autónoma del Estado de Morelos, Av. Universidad 1001, Col. Chamilpa 62210, Cuernavaca, Mor., Mexico, fax + 52 (777) 329-7997, e-mail: myolanda@uaem.mx. Published in *Khimiya Prirodnykh Soedinenii*, No. 3, pp. 240-241, May-June, 2005. Original article submitted October 29, 2004.

were measured on a JEOL JMS-AX 505 HA mass spectrometer. Electron impact mass spectra were obtained at 70 eV ionization energy.

**Plant Material.** The leaves of *A. pennatula* were collected in January 2001 at Chamilpa, Cuernavaca, Morelos, Mexico. The botany specimen (voucher 10329) was identified by Dr. Oscar Dorado and deposited at the Herbarium of the Universidad Autonoma del Estado de Morelos (HUMO), Cuernavaca, Morelos, Mexico.

**Extraction and Isolation.** The dried and powdered leaves (2.0 kg) of *A. pennatula* were exhaustively extracted with acetone (3 × 10 L) at room temperature to yield 178 g of residue. This extract was chromatographed on CC over silica gel 60 (600 g), using a gradient of *n*-hexane–acetone as eluent. The composition of the obtained fractions (500 mL each) was monitored by TLC, and the chromatographically identical fractions were combined, yielding four groups: G-1 [3.6 g, *n*-hexane 100%], G-2 [16.8 g, *n*-hexane–acetone, 90:10], G-3 [1.5 g, *n*-hexane–acetone, 80:20], and G-4 [2.6 g, *n*-hexane–acetone, 70:30]. Each group was further separated using CC over silica gel 60, and a gradient of *n*-hexane–acetone as eluent. Fraction G-1 yielded triacontanol [3] (568 mg, 0.32% yield with respect to dried extract) and lupenone [8] (726 mg, 0.41%); fraction G-2 yielded  $\beta$ -sitosterol palmitate [4] (946 mg, 0.53%), squalene [5] (168 mg, 0.09%), lupeol [9] (352 mg, 0.20%), nonaprenol [6] (167 mg, 0.09%), and  $\beta$ -sitosterol (416 mg, 0.23%); fraction G-3 yielded norphytane [7] (**1**, 128 mg, 0.07 %) and fraction G-4 yielded daphnetin [10] (864 mg, 0.49%) and catechin [11] (312 mg, 0.18%). Plant material was further exhaustively extracted with methanol (3 × 10 L) at room temperature to yield 234 g of residue. This extract was chromatographed on CC over silica gel 60 (800 g), using a gradient of *n*-hexane–acetone as eluent. The chromatographically identical fractions were combined, yielding three groups: G-5 [4.40 g, *n*-hexane–acetone, 70:30], G-6 [1.75 g, *n*-hexane–acetone, 60:40], and G-7 [6.5 g, *n*-hexane–acetone, 50:50]. Each group was further separated using CC over silica gel 60, using a gradient of *n*-hexane–acetone as eluent. Fraction G-5 yielded catechin [11] (622 mg, 0.27%); fraction G-6 yielded catechin [11] (119 mg, 0.05%), daucasterol [13], and stigmasteryl- $\beta$ -D-glucopyranoside [14]; and fraction G-7 yielded epigallocatechin [11] (19 mg, 0.008%) and eriodictyol [12] (95 mg, 0.04%).

## ACKNOWLEDGMENT

This work was financially supported by CONACyT (Project No. 40405).

## REFERENCES

1. J. B. Harborne, D. Boulter, and B. L. Turner, *Chemotaxonomy of the Leguminosae*, Academic Press, London, N. Y., 1971.
2. J. Popoca, A. Aguilar, D. Alonso, and M. L. Villarreal, *J. Ethnopharmacol.*, **49**, 173 (1998).
3. M. A. Nogueira, J. S. Oliveira, and S. Ferraz, *Phytochemistry*, **42**, 997 (1996).
4. B. E. Nielsen and H. Kofod, *Acta Chem. Scand.*, **17**, 1161 (1963).
5. L. Pogliani, M. Ceruti, G. Ricchiardi, and D. Viterbo, *Chem. Phys. Lipids*, **70**, 21 (1994).
6. Y. Tanaka, H. Sato, and A. Kageyu, *Polymer*, **23**, 1087 (1982).
7. R. A. Goodman, E. Oldfield, and A. Allerhand, *J. Am. Chem. Soc.*, **95**, 7553 (1973).
8. R. C. Carpenter, S. Sotheeswaran, M. U. S. Sultanbawa, and B. Ternai, *Org. Magn. Reson.*, **14**, 462 (1980).
9. D. Burns, W. F. Reynolds, G. Buchanan, P. B. Reese, and R. G. Enriquez, *Magn. Reson. Chem.*, **38**, 488 (2000).
10. N. J. Cussans and T. N. Huckerby, *Tetrahedron*, **31**, 2719 (1975).
11. A. L. Davis, Y. Cai, A. P. Davies, and J. R. Lewis, *Magn. Reson. Chem.*, **34**, 887 (1996).
12. C. Moretti, M. Sauvain, C. Lavaud, G. Massiot, J.-A. Bravo, and V. Munoz, *J. Nat. Prod.*, **61**, 1390 (1998).
13. S. Faizi, M. Ali, R. Saleem, and I. S. Bibi, *Magn. Reson. Chem.*, **39**, 399 (2001).
14. M. S. Alam, N. Chopra, M. Ali, and M. Niwa, *Phytochemistry*, **41**, 1197 (1996).
15. a) B. Hallgren and S. Larsson, *Acta Chem. Scand.*, **17**, 543 (1963); b) T. C. Jain, R. J. Striha, *Can. J. Chem.*, **47**, 4359 (1969).
16. a) E. Malan, *Phytochemistry*, **33**, 733 (1993); b) M. Ali, A. Heaton, and D. Leach, *J. Nat. Prod.*, **60**, 1150 (1997); c) T.-H. Lee, F. Qiu, G. R. Waller, and Ch.-H. Chou, *J. Nat. Prod.*, **63**, 710 (2000).