Cano, Arturo; Bucio, José Luis; Espinoza, Marina; Ruíz Cancino, Alejandro
Sesqui- and Tri- Terpenoids from Esenbeckia species (Rutaceae)
Sociedad Química de México
Distrito Federal, México

Available in: http://www.redalyc.org/articulo.oa?id=47544219
Investigación

Sesqui- and Tri-Terpenoids from Esenbeckia species (Rutaceae)

Arturo Cano,* José Luis Bucio, Marina Espinoza and Alejandro Ruíz-Cancino†

Facultad de Estudios Superiores Zaragoza, Universidad Nacional Autónoma de México. Av. Guelatao No. 66 (Eje 7 Oriente). Col. Ejército de Oriente. Iztapalapa 09230, México D. F. Email: caf6205@prodigy.net.mx. Teléfono: 5623-0758

Recibido el 18 de marzo del 2000; aceptado el 16 de junio del 2000

In memoriam to Dr. Jacobo Gómez-Lara

Abstract. Three *Esenbeckia* species (Rutaceae) were chemically analyzed by means of conventional chromatographic, spectroscopic and spectrometric techniques. From the aerial parts of *E. berlandieri* ssp *berlandieri* were obtained friedelin, β-sitosterol, and β-sitosteryl-β-D-glucoside. Limonin was characterized as the main constituent from the seeds of *Esenbeckia ovata*. From the aerial parts of *E. velutinosa* friedelin, caryophyllene β-oxide, lupeol, lupenone, cryptomeridol and β-sitosterol were isolated and characterized.

Key Words: *Esenbeckia berlandieri* ssp. *berlandieri*, *E. ovata*, *E. velutinosa*, Rutaceae, sesquiterpenes, triterpenes, limonin.

Results and Discussion

From the aerial parts of *E. berlandieri* ssp *berlandieri* were isolated and identified friedelin [15], β-sitosterol and β-sitosteryl-β-D-glucoside. From the seeds of *E. ovata* was isolated a white solid that exhibited positive reaction in the Ehrlich test for furanes [16], whose presence was according to the signals at δ 7.42 (2H, s, H-21, H-23) in the 1H NMR spectrum, and was confirmed by the fragment at m/z 95 in the EIMS. The presence of an AB system centered at δ 4.92 (1H, J = 13 Hz) and δ 4.48 (1H, J = 13 Hz) in the 1H NMR spectrum is characteristic for an oxygenated function at C-19 of polycyclic modified triterpenes, according to the molecular formula C_{30}H_{38}O_4 determined by EIMS. The presence of an α, β-epoxy-δ-lactone in the D-ring was established by the signals at δ 5.47 (H-17) y δ 4.04 (H-15), suggesting a limonoid-type substance. COSY experiments allowed the assignments of the signals at δ 2.68 (dd, J = 16.8, 2.1) and δ 2.98 (dd, J = 16.8, 3.9 Hz) for the hydrogens α to the carbonyl group in the A-ring, while those at δ 2.86 (t, J = 15) and δ 2.47 (dd, J = 15, 3.5 Hz) corresponded to the hydrogens at C(6). The methyl signals at δ 1.30, 1.18, 1.17 and 1.08 were assigned to CH_{3}-18, CH_{3}-25, CH_{2}-26 and CH_{3}-24, respectively, confirming the structure of limonin A (I) for this secondary metabolite [17]. Friedelin, β-sitosterol, lupeol [18], cryptomeridol [19], lupenone and caryophyllene epoxide [20] were isolated from the aerial parts of *E. velutinosa* and identified by direct comparison with authentic samples.

These results along with those previously reported [3-14] indicate that *Esenbeckia* species biosynthesize different structural types of secondary metabolites. Additional chemical studies of other species are necessary in order to establish the chemotaxonomic significance of the isolated substances.
Experimental

*Esenbeckia berlandieri* ssp *berlandieri* ex Hemsley was collected in the state of Veracruz. A voucher specimen is deposited at the National Herbarium (MEXU, CHR-30).

The seeds of *E. velutinosa* (940 g; collected in the state of Veracruz, provided by Prof. C.H. Ramos (sp. nov.) (1.8 kg, provided by C. H. Ramos and deposited at the National Herbarium) were macerated with acetone. The crude extract (62 g) was adsorbed onto silica gel and carefully chromatographed on a silica gel column at reduced pressure (VLC) [21] eluting with *n*-hexane and *n*-hexane containing increasing proportions of EtOAc. This procedure allowed the isolation of friedelin (250 mg) [15], β-sitosterol (220 mg), lupeol (22 mg) [18]. Elution with *n*-hexane-EtOAc (3:2) afforded 3.45 g of a residue, which was rechromatographed at reduced pressure (VCC) and some fractions (TLC control) were further purified by prep. TLC (silica gel, *n*-hexane-AcOEt, 5:9), to give cryptomeridiol (19 mg) [19]. The mother liquors from the isolation of friedelin, were rechromatographed via VLC using *n*-hexane as eluent, to give lupenone (20 mg) and caryophyllene (11 mg) [19]. All the substances were identified by direct comparison with authentic samples.

The seeds of *E. ovata* Brandegee (940 g; collected in the state of Veracruz, provided by Prof. C.H. Ramos, key: CHR 32) were extracted with *n*-hexane and then with CHCl₃ at room temp. affording 63.4 g of residue. The crude CHCl₃ was adsorbed onto silica gel and analyzed via liquid chromatography (VLC) [21], the chromatographic fractions were rechromatographed at reduced pressure (VLC) [21], eluting with *n*-hexane and *n*-hexane containing increasing proportions of EtOAc. This procedure allowed to isolate friedelin (240 mg), β-sitosterol (100 mg) and mixtures of β-sitosterol-β-D-glucoside (390 mg).

**Friedelin.** White crystals, mp 245-247°C [15]; IR (CHCl₃): 3457, 3308, 3239, 3164, 3064, 2958, 2876, 1753, 1284, 1028 cm⁻¹; 1H NMR (CDCl₃, 300 MHz): δ 0.72 (3H, s, CH₂-27), 0.85 (3H, d, CH₂-23), 0.87 (3H, s, CH₃-29), 0.95 (3H, s, CH₃-24), 1.0, 1.18 y 1.25 (9H, s, CH₃-25, CH₃-26, CH₃-28), 2.25 (1H, c, J = 7 Hz, H-4), 2.42 (1H, dd, J = 5 Hz, H-2), 2.38 (1H, dd, J = 5, 2 Hz, H-2); EMIE m/z (rel. int.): 426 [M⁺] (29), 302 (8169, 274 (22), 273 (8379, 246 (25), 218 (8299, 205 (824), 191 (77), 179 (32), 164 (36), 125 (59), 123 (60), 121 (40), 109 (77), 96 (852), 95 (100), 81 (60), 69 (62), 55, 93).

Acknowledgements

The authors are grateful to M. Sc. Clara H. Ramos (Instituto de Biología, UNAM) for the supply and identification of plant material, to M. Sc. María Isabel Chávez, Beatriz Quiroz, Rocío Pañino, Luis Velasco and Francisco J. Pérez Flores from Instituto de Química de la UNAM for technical assistance, and Dr. Guillermo Delgado for stimulating interest and support to this work. We also thank to Carrera de Biología and Coordinación de Investigación de la FES-Zaragoza (UNAM) for partial financial support.

References

Sesqui- and Tri-Terpenoids from *Esenbeckia species* (Rutaceae)