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Antonio G. González, Javier G. Luis, Lucia San
Andrés, José J. Mendoza, and Angel G. Ravelo

J. Nat. Prod., **1991**, 54 (2), 585-587 • DOI:
10.1021/np50074a038 • Publication Date (Web): 01 July 2004

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Chemical Society, 1155 Sixteenth Street N.W., Washington,
DC 20036

A NEW FRIEDOOLEANE TRITERPENIC ACID FROM *SCHAEFFERIA CUNEIFOLIA*

ANTONIO G. GONZÁLEZ, JAVIER G. LUIS,* LUCIA SAN ANDRÉS,
JOSÉ J. MENDOZA, and ANGEL G. RAVELO

Centro de Productos Naturales Orgánicos Antonio González, Universidad de La Laguna, Carretera La Esperanza 2,
La Laguna, 38206 Tenerife, Canary Islands, Spain

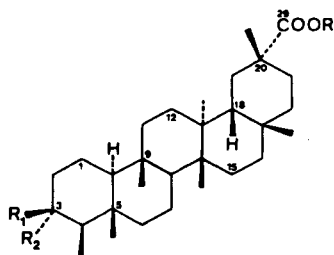
ABSTRACT.—A new minor friedooleane triterpenic acid has been obtained from polar fractions of a root extract of *Schaefferia cuneifolia* and its structure established as 2-oxofriedoolean-3-en-29-oic acid **6** from its spectral data and partial synthesis from polpunonic acid.

As part of an ongoing study of the chemical composition of flora used in Latin American folk medicine, *Schaefferia cuneifolia* A. Gray (Celastraceae) was re-examined (1,2). This species grows in northern Mexico and has shown activity in the treatment of venereal disease. An extract of the aerial part of the plant had previously yielded four new Δ^{18} -oleane triterpenes (3), while five new dihydro- β -agarofuran sesquiterpenes were isolated from the roots (4) together with two known triterpene quinones, pristimerin and tingenone (1). A new minor friedooleane triterpenic acid has now been obtained from more polar fractions of the same root extract, and its structure has been established as 2-oxofriedoolean-3-en-29-oic acid **6** from its spectral data and partial synthesis from polpunonic acid.

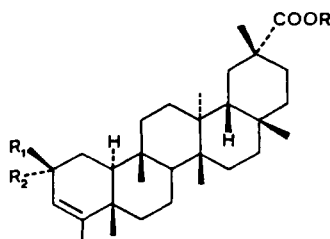
Compound **6**, $C_{30}H_{46}O_3$ by hreims (70 eV), when treated with CH_2N_2 gave a monomethyl ester **7** with ester (1720, 1240 cm^{-1}) and enone (1650 cm^{-1})

bands in its ir spectrum. In the 1H -nmr spectrum of **7**, signals appeared for six angular methyls, a methyl on an sp^2 hybridized carbon atom as a three-proton singlet at δ 1.92, and a vinyl proton as a broad singlet at δ 5.68, which was ascribed to the α proton of an α,β -unsaturated ketone. The above data suggested a friedooleane-skeleton triterpenic acid with an enone system in ring A. The ms fragmentation of both the acid and its methyl ester agrees with this characterization (5) and positions the carboxyl group on the C-29 or C-30 of ring E. Comparison of the ^{13}C -nmr spectra of friedelin (6), polpunonic acid (7), and **7** made it possible to assign the chemical shifts of all the carbons. The shift of 16.1 ppm for C-27 is compatible (8) with an α position for the carbomethoxy group on C-20.

The structure of **6** was confirmed by chemical means when the $NaBH_4$ reduction of polpunonic acid methyl ester [2], isolated as a free acid from the *n*-hexane



- 1 R = H; $R_1, R_2 = O$
- 2 R = Me; $R_1, R_2 = O$
- 3 R = Me, $R_1 = OH, R_2 = H$
- 4 R = Me, $R_1 = H, R_2 = OH$



- 5 R = Me, $R_1 = R_2 = H$
- 6 R = H; $R_1, R_2 = O$
- 7 R = Me; $R_1, R_2 = O$

extract of the aerial part of the same plant, gave a mixture of the epimeric alcohols **3** (9) and **4**. Dehydration of **3** with SOCl_2 in pyridine gave the alkene **5** which, when oxidized with CrO_3 in HOAc , yielded a product with physical and spectral data superimposable upon those of the methyl ester **7** obtained by treating **6** with CH_2N_2 .

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—General procedures were as previously described (4).

PLANT MATERIAL.—The plant was collected in northeastern Mexico and a voucher specimen, No. 7489, is on file with the Herbarium of the Department of Botany, Instituto Tecnológico y de Estudios Superiores de Monterrey, Mexico.

ISOLATION PROCEDURES.—Extraction and chromatography of the extract were carried out in the same way as described in our previous paper on the same plant (4). Part (4.7 g) of the hexane extract of the roots of *S. cuneifolia* was then repeatedly chromatographed on Si gel and afforded 2-oxofriedoolean-3-en-29-oic acid [**6**] (8 mg).

2-OXOFRIEDOOLEAN-3-EN-29-OIC ACID [6].—Compound **6** was obtained as a crystalline solid: hreims $[\text{M}]^+ m/z$ 454.3436 (calcd for $\text{C}_{30}\text{H}_{46}\text{O}_3$, 454.3426); ^1H nmr (CDCl_3 , 200 MHz) δ 0.91, 0.98, 0.98, 1.10, 1.13, 1.19 (3H each, s, Me-24, Me-25, Me-26, Me-27, Me-28, Me-30), 1.92 (3H, s, Me-23), 2.37 (2H, overlapping, H- α , H- β), 5.68 (1H, s, H-3); eims m/z (rel. int.) $[\text{M}]^+$ 454 (7), 300 $[\text{M}-154]^+$ (6), 285 $[\text{M}-169]^+$ (8), 271 $[\text{M}-183]^+$ (18), 250 (11), 246 (9), 245 (9), 235 $[\text{M}-219]^+$ (6), 231 (29), 229 (15), 205 (14), 203 (10), 191 $[\text{M}-263]^+$ (18), 189 (24), 187 (12), 177 (10), 175 (16), 163 (28), 161 (21), 149 (29), 137 (22), 135 (40), 133 (18), 123 (38), 121 (49), 108 (89), 107 (47), 95 (64), 93 (50), 81 (71), 67 (64), 55 (100).

2-OXOFRIEDOOLEAN-3-EN-29-OIC METHYL ESTER [7].—Compound **6** (8 mg), dissolved in Et_2O , was treated with an ethereal solution of CH_2N_2 to give the corresponding methyl ester **7** in good yield: mp 204–206°; $[\alpha]_D -2.60^\circ$ ($c=0.08$, CHCl_3); hreims $[\text{M}]^+$ at m/z 468.3617 (calcd for $\text{C}_{31}\text{H}_{48}\text{O}_3$, 468.3631); ir ν max cm^{-1} 2920, 1720, 1650, 1450, 1370, 1240, 1200; ^1H nmr (CDCl_3 , 200 MHz) δ 0.79, 0.86, 0.97, 1.07, 1.09, 1.17 (3H each, s, Me-24, Me-25, Me-26, Me-27, Me-28, Me-30), 1.86 (3H, d, $J=1.22$ Hz, Me-23), 3.62 (3H, s, $-\text{CO}-\text{OCH}_3$), 5.66 (1H, br s, H-3); ^{13}C nmr (CDCl_3 , 200 MHz) δ 37.8 (C-1), 201.0 (C-2), 125.6 (C-3),

172.5 (C-4), 29.1 (C-5), 34.4 (C-6), 18.1 (C-7), 50.1 (C-8), 37.2 (C-9), 56.0 (C-10), 34.5 (C-11), 30.3 (C-12), 39.4 (C-13), 40.2 (C-14), 30.1 (C-15), 36.3 (C-16), 30.5 (C-17), 44.7 (C-18), 29.4 (C-19), 40.7 (C-20), 29.8 (C-21), 36.6 (C-22), 18.4 (C-23), 19.2 (C-24), 17.5 (C-25), 19.0 (C-26), 16.1 (C-27), 32.0 (C-28), 179.3 (C-29), 32.1 (C-30), 51.7 (C-31); eims m/z (rel. int.) $[\text{M}]^+$ 468 (15), 395 (20), 300 (29), 285 (20), 272 (47), 264 (28), 255 (5), 249 (20), 231 (61), 223 (23), 189 (51), 169 (70), 135 (48), 121 (52), 109 (100), 81 (52), 67 (46), 55 (57).

NaBH₄ REDUCTION OF 2.—Methyl ester **2** (30.5 mg) prepared from **1** with CH_2N_2 was dissolved in MeOH (200 ml) and treated at room temperature with NaBH_4 (3 mg) while being stirred. After 2 h, the crude reaction was taken to dryness with a rotary vacuum evaporator, poured over H_2O , acidified with 5% HCl, thrice extracted with Et_2O , and chromatographed to yield **3** (26.2 mg) and **4** (2.3 mg).

3 α -HYDROXYFRIEDOOLEAN-29-OIC METHYL ESTER [4].—Compound **4** was obtained as an amorphous white solid: ^1H nmr (CDCl_3 , 200 MHz) δ 0.75, 0.81, 0.81, 0.83, 0.90, 1.06 (3H each, s, Me-24, Me-25, Me-26, Me-27, Me-28, Me-30), 0.85 (3H, d, $J=7.8$ Hz, Me-23), 3.30 (1H, m, H-3), 3.64 (3H, s, COOCH_3); eims m/z (rel. int.) $[\text{M}]^+$ 472 (4), 454 (28), 440 (16), 439 (32), 305 (6), 278 (15), 275 (25), 264 (41), 257 (38), 233 (21), 223 (26), 202 (27), 189 (45), 177 (22), 169 (67), 147 (40), 109 (100), 93 (52), 81 (70), 69 (53).

FRIEDOOLEAN-3-EN-29-OIC ACID METHYL ESTER [5].—Compound **3** (26.2 mg) dissolved in dry pyridine was chilled in an ice-bath, and SOCl_2 (5 drops) was added slowly. After 5 min, the mixture was poured over ice and extracted with EtOAc in the usual way, and after chromatographic purification it gave **5** (18.9 mg): mp 225°; $[\alpha]_D +27.77^\circ$ ($c=0.37$, CHCl_3); m/z $[\text{M}]^+$ 454.3795 (calcd for $\text{C}_{31}\text{H}_{50}\text{O}_2$, 454.3779); ir ν max cm^{-1} 2940, 2860, 1720, 1460, 1445, 1380, 1370, 1170, 1140; ^1H nmr (CDCl_3 , 200 MHz) δ : 0.80, 0.85, 0.85, 1.00, 1.06, 1.19 (3H each, s, Me-24, Me-25, Me-26, Me-27, Me-28, Me-30), 1.52 (3H, s, Me-23), 3.62 (3H, s, COOCH_3), 5.14 (1H, br s, H-3); eims m/z (rel. int.) $[\text{M}]^+$ 454 (60), 439 (48), 395 (17), 345 (11), 318 (19), 262 (69), 249 (34), 215 (20), 189 (49), 149 (40), 121 (80), 109 (98), 95 (100), 93 (70), 81 (75), 67 (56), 55 (74).

OXIDATION OF 5 WITH CHROMIC ACID.—Compound **5** (5.6 mg) dissolved in HOAc was treated with a few drops of a solution of CrO_3 in HOAc , stirred for 1 h at room temperature and then for 5 h at 40°. It was recovered upon addition of H_2O , extraction with CHCl_3 , and chromatography, to give **7** (2.3 mg).

ACKNOWLEDGMENTS

This research project has been subsidized by the CICYT, grant number FAR88-0501 and A.I.E.T.I.

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Received 24 May 1990