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TERPENOIDS FROM *MORTONIA DIFFUSA*

MARIANO MARTÍNEZ V.,* MIGUEL MUÑOZ CORONA, CRISTINA SÁNCHEZ VÉLEZ, LYDIA RODRÍGUEZ-HAHN,

Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, Coyoacán 04510, México, D.F.

and PEDRO JOSEPH-NATHAN

Departamento de Química, Centro de Investigación y de Estudios Avanzados, Instituto Politécnico Nacional, Apartado 14-740, 07000 México, D.F., México

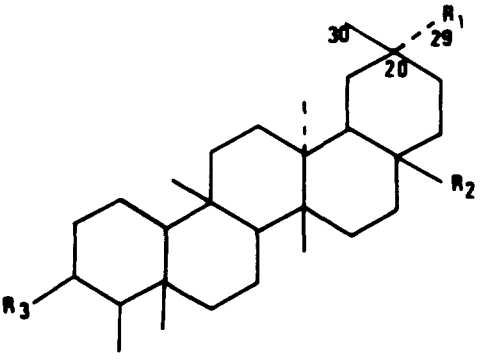
In continuation of our chemotaxonomic study of the genus *Mortonia* (Celastraceae) (1–3), we investigated *Mortonia diffusa* Rose and Standl, a shrub which grows in the semidesert areas of Puebla, México. The roots of *M. diffusa* and *Mortonia palmerii* have been used for the treatment of venereal infections (4).

The compounds isolated from *M. diffusa* are mortonin A and C (1–3) and the triterpenes lupeol (5), lup-20(29)-en-3β,30-diol (5), friedelan-3-one-29-al [**2**] (6), friedelan-3-one-29-ol [**3**] (6), and friedelan-3-one-29-oic acid [**4**] (6). This is the first time that **2** has been isolated from a natural source. Furthermore, comparison of the spectral and physical data of friedelan-3β,29-diol [**5**], obtained by reduction of **3**, with those reported for a compound considered to be friedelan-3β,28-diol [**8**], isolated from *M. palmerii* (7), led us to reassign the structure of the latter as **5**.

Mortonin A and C have been isolated from all the previously studied species of *Mortonia* (1–3); therefore, we confirm that their presence is a diagnostic feature for the inclusion of a species into the genus (1–3).

The isolation of the natural products was achieved by chromatographic methods, using Si gel and solvents of increasing polarity (see Experimental). Mortonin A and C were compared with authentic samples (1–3).

The spectral and physical data of lupeol and of lup-20(29)-en-3β,30-diol are identical to those published (5,6). In



	R_1	R_2	R_3
1	Me	Me	O
2	CHO	Me	O
3	CH_2OH	Me	O
4	CO_2H	Me	O
5	CH_2OH	Me	OH
6	CO_2Me	Me	O
7	CH_2OAc	Me	O
8	Me	CH_2OH	OH
9	CH_2OAc	Me	OAc

addition the physical and spectral data of **4** and of its methyl ester **6**, prepared using CH_2N_2, are identical to those of polpunonic acid and its methyl ester (6), respectively. A chemical correlation of **2**, **3**, and **4** was achieved using Jones reagent and established the structures of **2** and **3** (see Experimental).

Recently (8) it has been shown that the acid **4** and its methyl ester **6** adopt chair-chair conformations for the D/E rings, while the parent hydrocarbon friedelin [**1**] adopts a boat-boat conformation. The argument is that the repulsion between the methyl groups C-27 and C-29, which is responsible for the boat-boat conformation of the D/E rings in **1**, is released when C-29 is oxidized to a carbonyl group, and, thereby, the molecule can adopt a chair-chair conformation. The change in conformations can be detected from the ^{1}H-nmr spectra, since both groups (C-26 and C-27) appear more shielded in a chair-chair conformation, probably because C-27 is near to the shielding area of the carbonyl, while C-26 does not show the 1,4 interaction with C-28 that is present in a boat-boat conformation. Furthermore, a similar chemical shift difference for C-26 is reported for 16α-acetoxy-friedelane and its 16β epimer (10). Such difference can also be explained, because if the 16α compound had a boat-boat conformation, then the acetate moiety would be located very close to C-27. Therefore, the molecule adopts a chair-chair conformation.

Inspection of the ^{1}H-nmr spectra of **2**, **3**, and **7** (Table 1) reveals a chair-chair conformation for the aldehyde **2** and boat-boat conformations for the alcohol **3** and its acetate **7**. These results show that the conformational change arises simply upon transformation of the primary alcohol to an aldehyde.

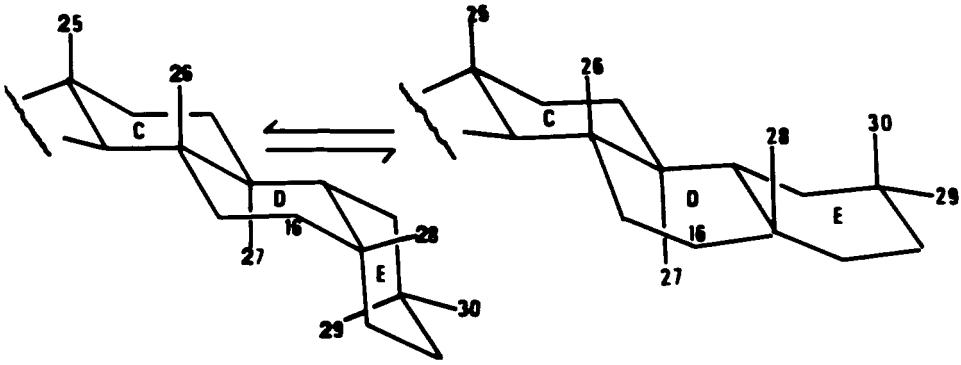


TABLE 1. ^{1}H-nmr Chemical Shifts at 300 MHz.

Proton	Compound					
	1[a]	2	3	4	6	7
23β	0.88		0.88	0.87	0.87	0.875
24β	0.73	0.70	0.72	0.71	0.71	0.72
25β	0.88	0.85	0.87	0.88	0.86	0.87
26β	1.01	0.85	1.03	0.88	0.86	1.03
27α	1.05	0.85	1.04	1.00[b]	0.87	1.03
28β	1.18	1.00	1.06	1.09	1.07	1.06
29α	0.97					
30β	1.01	1.10	1.23	1.26	1.18	1.21

[a]Values are from Ramaiah *et al.* (9).

[b]This apparently abnormal value for C-27α has been exhaustively discussed in Ramaiah *et al.* (9).

On the other hand, the difference in the chemical shifts of the C-30 methyl group on going from **1** to **3** is mainly due to the effect of a hydroxyl group at C-29 and is similar to that between **1** and **7**. However, the difference between **1** and **2** is due both to the change of conformation of the D/E rings and to the presence of a carbonyl moiety at C-29. Therefore, the C-27 and C-30 methyl groups are shifted by the C-29 aldehyde group.

The assignments of the ^{13}C-nmr spectra of **3** and **7** were done with aid of APT experiments and by comparison with reported data (9). See Table 2.

Treatment of the alcohol **3** with $NaBH_4$ in THF gave the diol **5**, which shows physical constants and spectral data identical to those reported for a compound thought to be friedelin-3β,28-diol [**8**], isolated from *M. palmerii* (7). These data, together with those for the diacetate **9**, definitively require the reassignment of structure **8** as **5**.

TABLE 2. ^{13}C-nmr Chemical Shifts of **3** and **7** at 75.4 MHz.

Carbon	Compound	
	3	**7**
1	22.3	22.3
2	41.6	41.5
3	212.9	213.1
4	58.4	58.2
5	42.1	42.0
6	41.5	41.2
7	18.3	18.2
8	53.5	50.3
9	37.6	37.5
10	59.7	59.5
11	35.8	35.2
12	30.7	30.4
13	38.4	39.2
14	40.1	39.3
15	32.9	29.3
16	36.0	36.2
17	30.6	30.1
18	42.2	44.5
19	39.6	29.1
20	33.2	40.6
21	29.9	29.5
22	27.9	36.5
23	6.8	6.8
24	14.7	14.7
25	17.9	17.5
26	18.5	18.5
27	20.8	16.0
28	32.2	32.0
29	74.8	72.7
30	25.9	31.2

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Melting points are uncorrected. ^{1}H-nmr and ^{13}C-nmr spectra were taken in $CDCl_3$ with TMS as the internal reference. Column chromatography was carried out on Si gel (0.063–0.2 mm). The spray reagent for tlc was $H_2SO_4/Ce_2(SO_4)_3$.

ISOLATION OF THE TERPENES.—The aerial parts of *M. diffusa*, collected 4 km north of Nopala, Puebla, México, in November 1980 (voucher MEXU 346252 deposited at the Instituto de Biología Herbarium, UNAM) were finely cut and extracted with MeOH and concentrated in vacuo. The addition of H_2O to the MeOH extract, followed by extraction with $CHCl_3$, yielded a residue which was chromatographed on Si gel. The elution with hexane, hexane/C_6H_6, C_6H_6, and C_6H_6/EtOAc led to the isolation of mortonins A and C, lupeol, lup-20(29)-en-3β,30-diol (5), friedelan-3-one-29-al [**2**], friedelan-3-one-29-ol [**3**] (6), and friedelan-3-one-29-oic acid [**4**] (6).

FRIEDELAN-3-ONE-29-AL [**2**].—Mp 273–275°, ir ($CHCl_3$) ν max cm^{-1} 1706; ^{1}H nmr (80 MHz) 9.4 (s, 1H, H-29), 1.10 (s, 3H, H-30), 1.00 (s, 3H, H-28), 0.85 (s, 9H, H-25, H-26, H-27), 0.86 (d, J = 6.5 Hz, 3H, H-23), 0.70 (s, 3H, H-24); ms (70 eV) *m/z* (rel. int.) $[M]^+$ 440 (25), 420 (20), 273 (70), 431 (38), 139 (86), 109 (80), 95 (100), 81 (80).

METHYL ESTER **6**.—Treatment of **4** with an ethereal solution of CH_2N_2 afforded the methyl ester **6**, mp 222–224° [lit. (6) 225–226°].

PREPARATION OF **2** FROM **3**.—Following the procedure reported for the oxidation of 30-hydroxy-friedelan-3-one to the respective aldehyde (6), we obtained, after purification by cc, the aldehyde **2** (21 mg) after controlled oxidation of **3** (40 mg). The product is identical in all respects (mmp, co-tlc, ir, ms, ^{1}H nmr) with the natural aldehyde **2**.

PREPARATION OF **4** FROM **2**.—Oxidation of **2** with Jones reagent at room temperature afforded the acid **4**, which is identical to the natural product.

PREPARATION OF DIOL **5**.—Reduction of **3** with $NaBH_4$ in a THF solution gave **5**, mp 270–272° [lit. (7) 270–272°].

DIACETATE **9**.—Mp 250–251° [lit. (7) 250–253°].

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