A NOVEL TRISNORLUPANE, DIOSPYROLIDE, FROM *DIOSPYROS MARITIMA*

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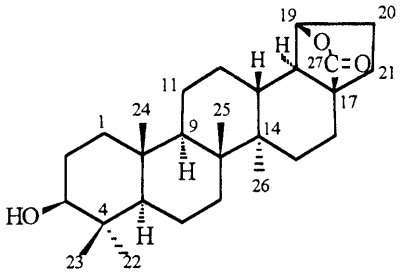
A novel trisnorlupane, diospyrolide, was isolated from the stem of *Diospyros maritima* Blume. The structure was elucidated by 2D NMR experiments and X-ray analysis.

KEY WORDS *Diospyros maritima*; trisnorlupane; diospyrolide; Ebenaceae; X-ray analysis

Thirteen species of *Diospyros* (Ebenaceae) are indigenous to Taiwan. Chemical studies of some species have been described,[1-6] and they contain triterpenes, lignans, steroids, benzoquinones, and naphthoquinones. The stems of *D. maritima* are usually used to treat rheumatic diseases, and it led us to study the chemical constituents. In a previous paper we reported four new naphthoquinone derivatives.[7] The further investigation of this extract led to the isolation of a novel trisnorlupane derivative, diospyrolide (**1**), together with two lupane derivatives, lupeol and lupenone. This paper deals with the structural elucidation of **1**.

Diospyrolide (**1**), mp 265~267°C, $[\alpha]_D^{25}$ = +30.8 ° (*c*=0.25, $CHCl_3$), has the molecular formula $C_{27}H_{42}O_3$ on the basis of the exact mass of HRFABMS [$(M+H)^+$ *m/z* 415.3212, calcd M^+ *m/z* 414.3136]. The IR absorption of hydroxyl and γ-lactone groups appeared at 3388 and 1764 cm^{-1}, respectively. The ^{1}H-NMR spectrum (Table 1) showed some readily assignable signals such as five methyl singlets (δ 0.98, 0.74, 0.82, 0.92 and 0.84), a carbinyl proton [δ 3.17 (dd, *J*=10.9, 5.3 Hz)], a methylene group [δ 1.88 (2H, t, *J*=7.0 Hz, H-20)], and a γ-H of lactone (δ 4.60, s). By comparison of the ^{13}C-NMR data with methyl betulinate,[8] compound **1** was considered to have a lupane skeleton with elimination of an isopropenyl moiety and with a γ-lactone group linked between C-17 and C-19. The EIMS fragmentation ion peaks of **1** at *m/z* 396 (M^+-H_2O, 100%), 381 (M^+-H_2O-CH_3,12%), 207 (52%), and 189 (82%) are typical of a lupane skeleton.[9] Detailed analysis of the ^{1}H-^{1}H COSY, HMQC, and HMBC spectra led to the assignment of **1**. NOESY correlations between H-3 and H-22, H-5 and H-22, Hβ-6 and H-24, Hα-7 and H-26, Hα-9 and H-26, Hβ-11 and H-25, H-13 and H-25, and Hβ-15 and H-20 were observed. The relative configuration of **1** was established by X-ray



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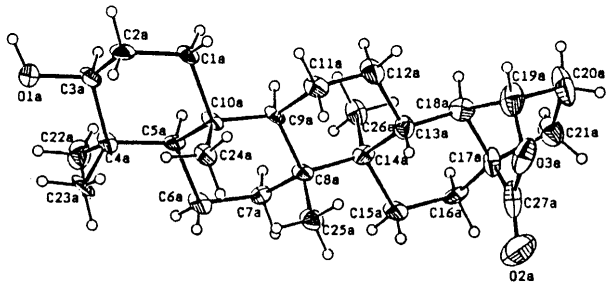

ORTEP drawing of **1**

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analysis. Compound **1** was crystallized in triclinic space group P1 with cell dimensions a=6.5045(20), b=7.185(3), c=28.143(6) Å, V=1178.8(7) $Å^3$, Z=2, F(000)=467, Dcalcd=1.193 $g·cm^{-3}$, μ=5.607 cm^{-1}, $2\theta_{max}$ =120.0, total measurement 3518 reflections, and crystal size 0.02, 0.25, and 0.50 mm. The crystal structure was solved by direct methods and was refined with the full-matrix least-square method.

Table 1 NMR data for **1** (^1H: 400 MHz and ^{13}C: 100 MHz in $CDCl_3$)

No.	δ H	δ C	HMBC	No.	δ H	δ C	HMBC
1	0.92,1.70	38.9	H-2,H-5,H-24	15	1.24,1.5	28.2	H-13,H-16,H-26
2	1.12,1.60	27.3	H-1,H-3	16	1.61	28.2	H-18,H-21
3	3.17	79.0	H-1,H-2,H-22,H-23	17		51.1	H-13,H-15,H-16,H-18,H-19,
4		39.0	H-2,H-6,H-22,H-23				H-20,H-21
5	0.68	55.4	H-6,H-7,H-22,H-23,H-24	18	1.52	55.0	H-12,H-13,H-16,H-20
6	1.38,1.52	18.2	H-5,H-7	19	4.60	79.2	H-13,H-18,H-20,H-21
7	1.39,1.41	34.1	H-5,H-6,H-9,H-25	20	1.88	29.6	H-19,H-21
8		40.6	H-6,H-9,H-11,H-13,H-25,	21	1.67	28.9	H-16,H-20
			H-26	22	0.98	28.0	H-23
9	1.28	51.0	H-1,H-11,H-12,H-25	23	0.74	15.3	H-3,H-5,H-22
10		37.3	H-1,H-2,H-5,H-24	24	0.82	16.4	H-1,H-9
11	1.29,1.49	20.6	H-9	25	0.92	15.6	H-7,H-9
12	1.50,2.05	22.2	H-11,H-13,H-18	26	0.84	13.1	H-13,H-15
13	1.51	34.2	H-11,H-12,H-15,H-18,H-26	27		179.5	H-16,H-18,H-19,H-21
14		40.6	H-9,H-12,H-13,H-15,H-18,				
			H-25,H-26				

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REFERENCES AND NOTES

1) Chou C. J., *Ann. Rep. Natl. Res. Inst. Chin. Med.*, **1984**, 117-140.
2) Chen C. C., Yu H. J., Huang Y. L., *Chin. Pharm. J.*, **44**, 229-233 (1992).
3) Chen C. C., Yu H. J., Ou J. C., Pan T. M., *J. Chin. Chem. Soc.*, **41**, 195-198 (1994).
4) Lee T. J., Shih T. S., Lin Y. M., Chen, F. C., *Formosan Sci.*, **38**, 147-151 (1984).
5) Chen H. C., Lin Y. M., Shih T. S., Chen F. C., *Formosan Sci.*, **41**, 46-52 (1987).
6) Chen H. K., Chen K. J., Lin Y. S., Chen F. C., *Formosan Sci.*, **44**, 63-71 (1991).
7) Kuo Y. H., Chang C. I, Kuo Y. H., *J. Chin. Chem. Soc.*, **43**, 511-514 (1996).
8) Wenkert E., Baddeley G. V., Burfitt I. R., Moreno L. N., *Org. Magn. Reson.*, **11**, 337-343 (1978).
9) Budzikiewicz H., Wilson J. M., Djerassi Carl, *J. Am. Chem. Soc.*, **85**, 3688-3699 (1963).

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