A Novel Triterpenoid of *Garcinia subelliptica*

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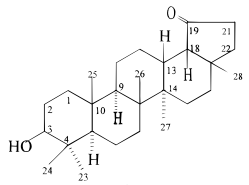
Received December 3, 1997

A novel lupane triterpene, 3β-hydroxy-20,29,30-trinorlupan-19-one, garcinielliptone (**1**), has been isolated from the seeds of *Garcinia subelliptica*.

Various constituents and antioxidant xanthones from the wood and root bark of *Garcinia subelliptica* Merr. (Guttiferae) have been reported.[1,2] In the search for biologically active constituents in Formosan Guttiferae plants, we investigated bioactive constituents of the seeds of *Garcinia subelliptica* and reported a novel triterpenoid compound, named garcinielliptin oxide.[3] In the continuing study of this plant, a novel lupane triterpenoid, 3β-hydroxy-20,29,30-trinorlupan-19-one, garcinielliptone (**1**), was isolated. In this paper we report the structure elucidation of **1**.



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The HRMS of **1** revealed a $[M]^+$ at *m/z* 400.3303, which corresponded to the molecular formula $C_{27}H_{44}O_2$. The IR spectrum of **1** showed hydroxyl and carbonyl absorption bands at 3495 and 1736 (five-membered ring ketone) cm^{-1}, respectively. The 27 carbon signals observed in the ^{13}C NMR spectrum were characterized by a DEPT experiment, which indicated that **1** was a triterpene having six methyls, 10 methylenes, five methines, and six quaternary carbons. The chemical shifts of one methine carbon signal (δ 78.9) and one quaternary carbon signal (δ 221.3) suggested the presence of hydroxyl and carbonyl groups. In addition, the ^{1} H NMR spectrum of **1** indicated six singlet methyl signals and one oxymethine proton signal, and the absence of isopropyl proton signals suggested that **1** was a lupane-, hopane-, or fernane-type triterpene with no isopropyl groups. In the HMBC spectrum, carbon signals resonating at δ 78.9, 38.8, and 55.2 were correlated with two methyl protons (δ 0.68 and 0.90), indicating that these signals were assignable to C-3, C-4, and C-5, respectively, and that the hydroxyl group was at C-3. Analysis of COSY 90 and HMQC spectra established the connectivity of a $^1H-^1H$ and $^1H-^{13}C$ spin system corresponding to an ethylene moiety (C-21 to C-22). In the HMBC spectrum, the carbon signal resonating at δ 221.3 was correlated with one methine proton (δ 1.79) and two methylene protons (δ 1.96 and 2.15), respectively, establishing connectivity between C-19 and C-18, and C-19 and C-21, with the carbonyl group at C-19. The other partial structures were detemined by correlations found in the $^1H-^1H$, COSY, HMQC, and HMBC spectra. In the NOESY spectrum, correlations between H-3α and Me-23, H-5 and H-9α, and H-9α and Me-27, suggested α-configurations for Me-23, H-5, and Me-27. The NOESY spectrum also indicated correlations between Me-26 and Me-25, and H-13 and H-18 and H-13, and Me-28, with no evidence of correlation between Me-25 and H-9α, or Me-26 and Me-27, suggesting β-configurations for Me-25, Me-26, H-13, H-18, and Me-28. The ^{13}C NMR assignments of **1** were made by performing ^1H-decoupled, DEPT, and 2D $^1H-^{13}C$ correlation experiments and by comparing the corresponding data of lupeol.[4] The ^{13}C NMR, HMBC, and three characteristic fragment ion peaks at *m/z* 163, 207, and 189 also supported structure **1**.[5] Thus, garcinielliptone (**1**) was characterized as 3β-hydroxy-20,-29,30-trinorlupan-19-one.

Experimental Section

General Experimental Procedures. Melting points are uncorrected. UV spectra were obtained on a JASCO UV−vis spectrophotometer, ^1H (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Varian Unity-400 spectrometer; IR spectra were recorded on a Hitachi model 260-30 spectrometer; MS were obtained on a JMS−HX 100 mass spectrometer.

Plant Material. The seeds of *Garcinia subelliptica* Merr. (Guttiferae) were collected at Kaohsiung, Taiwan, during July 1993, and were chipped and extracted with Me_2CO. A voucher specimen is deposited in our laboratory.

Extraction and Isolation. The Me_2CO extract was chromatographed over Si gel. Elution with cyclohexane−C_6H_6 (4:1) yielded **1** and garcinielliptin oxide.[3]

Garcinielliptone (1): colorless needles ($CHCl_3$), mp 269 °C, $[\alpha]^{26}_D$ +84 (*c* 0.1, $CHCl_3$); IR (KBr) ν_{max} 3495 (OH), 1736 (CO) cm^{-1}; ^1H NMR ($CDCl_3$, 400 MHz) δ 0.60 (1H, d, J = 9.4 Hz, H-5α), 0.68 (3H, s, Me-24), 0.74 (3H, s, Me-25), 0.77 (3H, s, Me-26), 0.90 (3H, s, Me-23), 0.95 (3H, s, Me-27), 1.08 (3H, s, Me-28), 1.15 (1H, m, H-9α), 1.21 (1H, m, H-13β), 1.79 (1H, d, J = 4.2 Hz, H-18β), 3.12 (1H, dd, J = 11.4, 4.9 Hz); ^{13}C NMR ($CDCl_3$, 100 MHz) δ 15.2 (C-27), 15.3 (C-24), 15.9 (C-26), 16.2 (C-25), 18.3 (C-6), 21.4 (C-11), 24.4 (C-28), 26.9 (C-22), 27.3

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S0163-3864(97)00547-8 CCC: $15.00
Published on Web 07/17/1998

(C-2 and C-15), 28.0 (C-23), 33.0 (C-7), 34.6 (C-16 and C-21), 35.6 (C-22), 37.1 (C-10), 38.2 (C-13), 38.7 (C-1), 38.8 (C-4), 40.9 (C-8), 41.6 (C-14), 41.8 (C-7), 50.7 (C-9), 55.2 (C-5), 57.4 (C-18), 78.9 (C-3), 221.3 (C-19); EIMS (70 eV) *m*/*z* $[M]^+$ 400 (2), 382 (6), 367 (5), 207 (47), 189 (66), 163 (15), 135 (50), 121 (51), 107 (60), 95 (75), 81 (84), 67 (77), 55 (92), 43 (100); HRMS *m*/*z* found 400.3303, calcd for $C_{27}H_{44}O_2$ 400.3341.

Acknowledgment. This work was supported by grant from the National Science Council of the Republic of China (NSC 86-2314-B-037-035).

References and Notes

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NP9705470