Garcinielliptin oxide, a triterpenoid with a novel skeleton, isolated from *Garcinia subelliptica*

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A novel triterpenoid, garcinielliptin oxide, is isolated from the seed of *Garcinia subelliptica* and determined by spectroscopic methods.

Various constituents and antioxidant xanthones from the wood and root bark of *Garcinia subelliptica* (Guttiferae) have been reported.[1,2] To search for biologically active compounds in Formosan Guttiferae plants, we investigated the constituents of the seed of *Garcinia subelliptica*. The seed of *G. subelliptica* was collected at Kaohsing, Taiwan, R.O.C. during July, 1993. The acetone extract was chromatographied over silica gel. Elution with cyclohexane–benzene (4 : 1) yielded garcinielliptin oxide **1**.

Compound **1**, a pale yellow oil showed $[\alpha]_D^{29}$ + 1 (c = 0.292, $CHCl_3$). High resolution MS revealed a $[M]^+$ at m/z 484.3191 which corresponded to the molecular formula $C_{30}H_{44}O_5$. Its ^1H NMR spectrum (Table 1) contained the signals of three γ,γ-dimethylallyl, two tertiary methyls, two secondary methyls, a methylene and two methine groups. The ^{13}C NMR spectrum (Table 1) of **1** further indicated the presence of 10 methyl, 4 methylene, 5 methine and 11 quaternary carbons.

Infrared absorption bands at 1780, 1750 and 1690 cm^{-1}, coupled with off-resonance singlets at δ 206.9, 209.0 and 217.6 in the ^{13}C NMR confirmed **1** contains three carbonyl groups. Analysis of HMQC, HMBC (Fig. 1) and COSY 90 spectra established the connectivities of the 1-oxopropyl group. The IR band and ^{13}C NMR spectra showed the presence of a tertiary alcohol (3325 cm^{-1}; δ 70.6). The above information in conjunction with the molecular formula showed the **1** to possess a *cis*-bicyclo [4.3.0] nonane moiety[3,4] with a hydroxy group in one of them.

Analysis of COSY 90 and HMQC spectra for **1** established the connectivities of four ^1H-^1H and ^1H-^{13}C spin systems corresponding to partial structures **a–d** (Fig. 1).

In partial structure **a** (Fig. 1), the HMBC of C-10 to H-11 to H-13 confirmed the connectivity of partial structure **a** to C-10. Additional HMBC from C-10 to H-6 and C-5 to H-21b and H-7b confirmed that the 1-oxopropyl group was linked to C-5 and C-5 fixed the connectivity between C-5 and partial structure **c**.

In partial structure **d**, the HMBC of C-8 to H-7a and H-26 and C-1 to H-7a and H-26 identified the connectivity between C-8 and partial structure **c** or **d**. The HMBC of C-1 to H-16a and H-16b; C-2 to H-16a and H-16b; and C-3 to H-16a confirmed that the partial structure **b** was linked to C-2 and showed connectivities to C-1 and C-3.

In addition to the above some key HMBC correlations and evidences, the HMBC of C-3 to H-14; C-4 to H-14 and H-15; C-9 to H-14 and OH; and C-5 to OH established the structure of garcinielliptin oxide as **1** (Fig. 1).

The ^1H and ^{13}C NMR spectra of **1** (Table 1) was assigned by COSY, HMQC, HMBC spectra and the ^{13}C NMR spectrum also assigned by comparison with those of *cis*-bicyclo [4.3.0] nonane.[5] The ^{13}C NMR spectra also supported the characterization of **1**.

This structure was also supported by the fragmentation pattern[6] of **1**.†

The relative configuration of **1** was determined by the phase-sensitive NOESY spectrum. The NOE correlations are illustrated by arrows in Fig. 2. To clarify the conformation of **1**

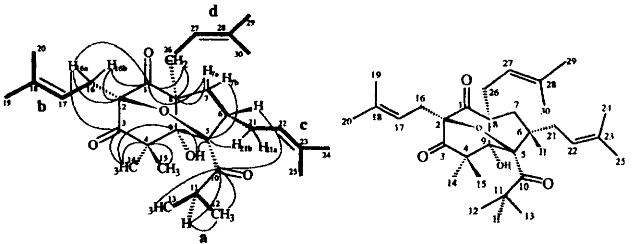

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Fig. 1 Structure of **1** and partial structure (**a–d**) of **1**, showing some key HMBC correlations. Bold lines represent ^1H-^1H and ^1H-^{13}C spin systems identified from COSY 90 and HMQC spectra.

Table 1 ^1H and ^{13}C NMR spectra of **1** (400 MHz, Me_4Si–$CDCl_3$)[a]

C		H	C		H	C		H
1	209.0		11	38.7	3.20 m	21	27.7	a 1.55 b 2.05 brd (12)
2	97.2		12	18.8	0.88 d (6.8)	22	122.1	4.92 m
3	206.9		13	17.0	1.09 d (6.8)	23	133.3	
4	44.0		14	17.7	α 0.94 s	24	25.8	1.69 s
5	107.9		15	23.0	β 1.23 s	25	17.9	1.55 s
6	40.8	β 0.95 m	16	23.7	a 2.49 dd (15.6, 6.8) b 2.74 dd (15.6, 6.8)	26	30.9	3.42 dd (13.2, 7.5) 3.42 dd (13.2, 7.5)
7	33.2	a 1.25 dd (14, 10) b 1.89 dd (14, 3.6)	17	116.0	5.10 m	27	118.9	5.27 m
8	54.8		18	135.8		28	133.7	
9	70.6	α-OH 8.10 s	19	25.8	1.64 s	29	26.0	1.69 s
10	217.6		20	17.9	1.63 s	30	17.6	1.57 s

[a] All assignments were confirmed by HMQC, HMBC and NOESY spectra data. Coupling constants (J in Hz) are given in parentheses.

(Fig. 1), a computer-assisted 3D structure (Fig. 2) was obtained using the molecular modelling program CHEM 3D V3.1 for Apple Macintosh, using MM2 force field calculations for energy minimization. One of the most stable conformations of **1** obtained from above further identified with the aid of the INSIGHT II‡ modelling system, using where possible, units from within the fragment library. Geometry optimization was performed using DISCOVER utilizing the CVFF (Consistent Valence Force Field) force field. The results were visualized using INSIGHT II running on a Silicon Graphics IRIS (SGI) INDIGO XS24–4000. The conformational search suggested the stable conformation as shown in Fig. 2.

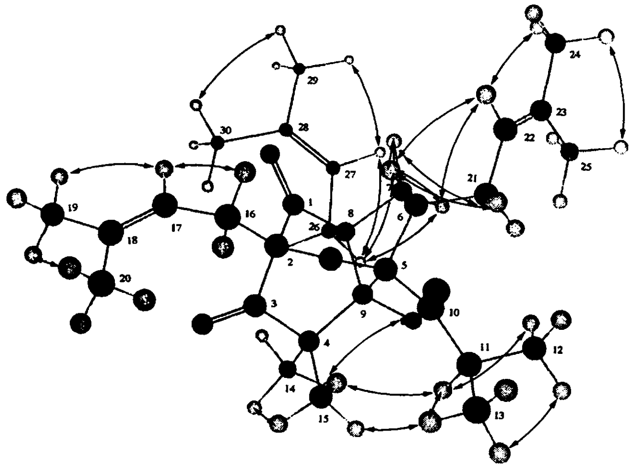

Fig. 2 Stereoview of **1** generated from computer modelling. The arrows show the NOE relationships.

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Footnotes

† *Mass spectroscopy* of **1**. *m*/*z* 484 (6%) M, 387 (26) M − [$Me_2CCHCH_2CO^+$], 359 (4) 387 − [CO], 345 (23) 387 − [C_3H_6], 331 (12) 359 − [CO], 319 (48) M − [$Me_2CCHCH_2CO^+$] − [CH_2CHCMe_2 + H], 251 (31) M − [$Me_2CCHCH_2CO^+$] − [CH_2CHCMe_2 + H] − [CH_2CHCMe_2 + H], 195 (21) M − [$Me_2CCHCH_2CO^+$] − 2 [CH_2CHCMe_2 + H] − 2 [CO].

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