# POLYISOPRENYLATED BENZOPHENONES FROM GARCINIA PEDUNCULATA

A. SAHU, B. DAS and A CHATTERJEE\*

Department of Pure Chemistry, University College of Science, 92 Acharya Prafulla Chandra Road, Calcutta 700 009, India

(Received 28 July 1988)

Key Word Index-Garcinia pedunculata, Guttiferae, polyisoprenylated benzophenones, pedunculol, garcinol, cambogin

**Abstract**—Pedunculol, a polyisoprenylated benzophenone derivative, together with two known polyisoprenylated benzophenones, garcinol and cambogin has been isolated from the pericarp of *Garcinia pedunculata*. The structure of the new compound was elucidated from spectral and chemical studies.

#### INTRODUCTION

A new polyisoprenylated benzophenone derivative, pedunculol (1) has been isolated from the methanol extract of the dried fruits of *Garcinia pedunculata* Roxb The structure of the compound was established through spectral and chemical studies Two other polyisoprenylated benzophenones, garcinol (2) and cambogin (3), have been isolated for the first time from this plant The structure of cambogin was established by X-ray crystallography

## **RESULTS AND DISCUSSION**

Pedunculol (1),  $C_{38}H_{52}O_6$  ([M]<sup>+</sup> m/z 604), mp 125° ( $C_6H_6$ ),  $[\alpha]_D^{25*}$  -159° (EtOH), was obtained as a pale yellow crystalline solid in poor yield (0.0014%) Its UV spectral data [ $\lambda_{max}^{EtOH}$  nm (log  $\varepsilon$ ): 353 (3.83), 277 (4 15) and 207 (4.43)] indicated it to be a polyisoprenylated benzophenone derivative [1-3] Its IR spectrum showed the presence of hydroxyl groups (3200-3500 cm<sup>-1</sup>) and three

carbonyl groups (1720, 1660, 1650 cm<sup>-1</sup>), two of which were conjugated The <sup>1</sup>H NMR spectrum of 1 in CDCl<sub>3</sub> was very similar to that of garcinol [2, 3]. The spectrum revealed the presence of an aromatic ABX system ( $\delta$  7.05. 1H, dd, J = 90 and 2.0 Hz; 6 91, 1H, d, J = 2.0 Hz and 6.65, 1H, d, J = 9.0 Hz), three vinyl protons ( $\delta 4.85$ , 4.80 and 4.76, each t, J = 5.0 Hz) and six vinyl methyl groups (8170, 1.68, 1.65, 158, 1.54 and 1.52, 3H each, s) Four saturated methyl groups appeared at  $\delta 1 \, 16$  (6H, s) and 1.02 (6H, d, J = 7.0 Hz) A complex multiplet was discernible in the region  $\delta 1.31-2.78$  showing the presence of 13 methylene and methine protons In the aliphatic region, the spectrum clearly showed the presence of three 3,3dimethylallyl units  $[-CH_2, CH=C(Me)_2]$ , one  $-C(Me)_2$ unit and one -CH(Me)<sub>2</sub> unit. The only significant difference between the <sup>1</sup>H NMR spectra of pedunculol (1) and garcinol (2) is the presence of a C-30 isopropenyl unit in the latter but not in the former. This establishes that the C-31(32) bond in 1 is saturated. A finding which was confirmed by the observation that pedunculol failed to



1233



Scheme 1

undergo acid catalysed cyclization to the corresponding dimethyl pyran derivative when refluxed with hydrochloric acid However, this reaction was extremely facile with garcinol (2) which readily underwent acid catalysed cyclization to cambogin (3)

The mass spectrum of 1 displayed two significant peaks at m/z 466 and 138 due to the fragments A and B These fragments were generated by cleavage of the C-8(29) bond with the migration of a hydrogen radical from C-30 to the oxygen at C-1 (Scheme 1)

From comparison of the <sup>1</sup>H NMR spectra together with the mass spectra of pedunculol ( $[M]^+$  604) and garcinol ( $[M]^+$  602) the structure of the former as 1 was finally settled The structure of pedunculol (1) was unambiguously assigned from the study of its 100 MHz <sup>13</sup>C NMR spectrum in CDCl<sub>3</sub> (Table 1) The signals were assigned from a DEPT experiment and the data compared with the reported values [2, 3] of the corresponding signals of garcinol (2).

In addition to pedunculol (1), two other polyisoprenylated benzophenones, garcinol (2) and cambogin (3), have also been isolated This is the first report of the isolation of the latter two compounds from this *Garcinia* species The structure of cambogin was confirmed by X-ray crystallographic analysis

## EXPERIMENTAL

Mps uncorr, Specific rotations CDCl<sub>3</sub> and EtOH, UV EtOH, IR KBr, <sup>1</sup>H NMR 400 MHz, CDCl<sub>3</sub> using TMS as an int standard, <sup>13</sup>C NMR 100 MHz, CDCl<sub>3</sub>, MS 70 eV

Plant material The fruits of Garcinia pedunculata were collected from Jorhat, Assam, India The pericarp of the fruits had a light violet colour A voucher specimen (Gp) has been preserved in our laboratory

Isolation of pedunculol, garcinol and cambogin The air-dried and coarsely powdered pericarp (2 kg) of G pedunculata were percolated with MeOH for 1 month The extract was concd under red pres at 40<sup>o</sup> and chromatographed over silica gel The column was eluated with solvents of increasing polarity The benzene eluates furnished a pale yellow solid which on crystallisation from benzene gave pedunculol (1), mp 125<sup>o</sup>, MS m/z 604 [M]<sup>+</sup>, 574, 466, 465, 357, 341, 287, 138

The later fractions of the C<sub>6</sub>H<sub>6</sub> eluate gave garcinol (2) which was crystallized from C<sub>6</sub>H<sub>6</sub>, mp 120° (lit [2] 122°),  $[\alpha]_{D}^{25}$ -142° (CHCl<sub>3</sub>), yield 0 0056%, UV  $\lambda_{max}^{LiOH}$  nm (log  $\varepsilon$ ) 363 (3 96) and 260 (4 09), IR  $\nu_{max}^{KBr}$  cm<sup>-1</sup> 3200-3500, 1720, 1660, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$  6 95 (1H, dd. J=90 and 20 Hz), 6 91 (1H, d, J = 20 Hz), 6 57 (1H, d, J=90 Hz), 4 94, 5 08, 5 02 (1H each, t, J = 50 Hz), 4 34 (d with finer splitting, J = 150 Hz), 2 75-1 42 (m,

 $12H_2 > CH_2$  and  $-C-H_1$ , 179, 174, 169, 165, 158, 153, 151,

Table 1 <sup>13</sup>C NMR spectral data of pedunculol (1) in CDCl<sub>3</sub>

C	δ	С	δ
1	195 3	20	26 4
2	116 3	21	25 7
3	195 5	22	184
4	658	23	18 5
5	49 5	24	36.8
6	46 8	25	1234
7	29 0	26	133.0
8	619	27	257
9	208 2	28	259
10	196 5	29	270
11	128.9	30	434
12	1161	31	43 8
13	143 2	32	178
14	149 4	33	18.2
15	1149	34	326
16	118 5	35	123 3
17	31.3	36	135 2
18	1236	37	256
19	1327	38	23 1

1 16, 1 00 (3H each, s, 9 × Me), MS m/z 602 [M]<sup>+</sup> 574, 533, 465, 341, 287, 231, 137

Cambogin (3) was isolated from the  $C_6H_6$ -EtOAc (1–1) eluate and crystallized from  $C_6H_6$ , mp 240° (lit [2] 242°),  $[\alpha]_D^{25} - 211°$ (EtOH), yield 0 007%, UV  $\lambda_{max}^{LtOH}$  nm (log  $\varepsilon$ ) 313 (4.07), 264 (4.41) and 228 (4.48), IR  $v_{max}^{RB}$  cm<sup>-1</sup> 3300–3450, 1710, 1680, 1670, <sup>1</sup>H NMR (CDCl<sub>3</sub>)  $\delta$ 7 39 (1H, *d*, *J* = 2 0 Hz), 7 15 (1H, *dd*, *J* = 9 0 and 2 0 Hz), 6 85 (1H, *d*, *J* = 9 0 Hz), 5 20 (1H, *t*, *J* = 5 0 Hz), 4 96 (2H, *t*, *J* = 5 0 Hz), 3 71–1 82 (12H, *m*,  $\gg$ CH<sub>2</sub> and -C-H), 1 67

and 1 53 (6H each, s,  $4 \times Me$ ), 1 78, 1 63, 1 26, 1 15, 0 98, 0 92 (3H each, s,  $6 \times Me$ ), MS m/z 602 [M]<sup>+</sup> 574, 533, 465, 449, 341, 325, 137

Reactions of pedunculol with HCl Pedunculol (50 mg), conc HCl (0 1 ml) and  $C_6H_6$  (20 ml) were refluxed for 12 hr [4] The compound remained unchanged as indicated by TLC and co-TLC

Reaction of garcinol with HCl Garcinol (100 mg), conc HCl (0 1 ml) and  $C_6H_6$  (25 ml) were refluxed for 2 hr EtOAc (25 ml) was added and the organic layer was separated, washed with  $H_2O$  (3 × 25 ml) and dried The solvent was removed under red pres when a gummy mass was obtained The residue on crystallization from  $C_6H_6$  afforded cambogin, mp 240°, yield 80%. The compound was found to be identical with the natural product in all respects (co-TLC, mmp and superimposable IR)

Acknowledgements—The authors express their sincere thanks to Professor T Prangé (University of Paris-Sud, France) for X-ray crystallographic analysis of cambogin, Dr H Ruegger, (Spectrospin, Switzerland) and Professor F. Bohlmann, (Institut fur Organische Chemie der Technischen Universitat, Berlin, Germany) for spectral measurements and to Sri P Ghosh and Sri J Ghosh of the Organic Instrumentation Laboratory, Department of Chemistry, Calcutta University for recording UV and IR spectra. Two of us (AS & BD) thank the University Grants Commission, New Delhi for financial assistance

#### REFERENCES

- 1 Karanjgaokar, C G., Rama Rao, A V., Venkataraman, K., Yemul, S S and Palmev, K J. (1973) Tetrahedron Letters 4977
- 2 Rama Rao, A V, Venkataswamy, G. and Pandse, A D (1980) Tetrahedron Letters 21, 1975
- 3. Krishnamurthy, N., Lewis, Y. S. and Ravindranath, B. (1981). Tetrahedron Letters 22, 793
- Rama Rao, A. V., Venkataswamy, G. and Yemul, S. S. (1980). Indian J. Chem. 19B, 627