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Large scale extraction of the fruits of *Garcinia indica* for the isolation of new and known polyisoprenylated benzophenone derivatives

Ranjeet Kaur, Sunil K. Chattopadhyay*, Sudeep Tandon, Shelly Sharma

Central Institute of Medicinal and Aromatic Plants (Council of Scientific and Industrial Research), Lucknow 226015, U.P., India

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ABSTRACT

Large scale extraction of the fruits of *Garcinia indica* was conducted with water extracted hydroxyl citric acid. The marc left after water extraction was extracted exhaustively with methanol and concentrated methanol. The concentrated methanol extract was adsorbed with celite and dried. The dried celite containing the methanol extract was successively extracted with hexane, chloroform and ethyl acetate to get hexane, chloroform and ethyl acetate extract respectively. Column chromatographic separation of hexane extract afforded two new molecules, one polyisoprenylated benzophenone and a new acylphloroglucinol derivative and two known molecule garcinol and isogarcinol. Likewise, chromatographic separation of the chloroform and ethyl acetate extract also yielded extra quantity of garcinol and isogarcinol respectively. Garcinol was isolated as a major compound among all the four molecules isolated from the fruits *G. indica*.

1. Introduction

Garcinia (family: Gutterferae) is a large genus of evergreen trees and shrubs distributed in tropical Asia, Africa and Polynesia. About thirty species occur in India (Anon., 1956). *Garcinia indica* is a slender evergreen tree with drooping branches. The fruits of *Garcinia* plants are globose or spherical in shape, dark purple when ripe enclosing five to eight seeds. In India, the tree is found in the tropical rain forests of Western Ghat from Konkan southwards in Mysore, Coorg and Wynaad. The fruits of *Garcinia* are anthelmintic, cardiotonic and useful in piles, dysentery, tumors, pains and heart complaints (Anon., 1956). The dried rind of *G. indica* is traditionally used as a garnish for curry. In Ayurveda, the drug has anthelmintic and cardiotonic properties. Decoction of the fruit is used in treatment of diabetes. The oils from the seeds of *Garcinia indica* are used in preparing chocolates, medicines, and cosmetics. Kokum butter is extracted from the seeds and used in the cosmetic industry for preparing lotions, creams, lip balms, and soaps (Padhye et al., 2009). Kokam is the pink sweet smelling welcome drink offered to world travelers spending summer holidays on the beautiful beaches of Goa in India to avoid skin damages and allergies from the sun and tropical climate. It is supposed to reduce degeneration of the skin cells and restore elasticity (Padhye et al., 2009). The fruit rind has also been utilized as a pink and purple food coloring agent and as a culinary spice to provide a sour and sweet taste to foods (Hong et al., 2007). The literature revealed the presence of polyisoprenylated benzophenone derivatives, namely garcinol, isogarcinol, xanthochymol, isoxanthochymol and organic acids chiefly contain (−)-hydroxycitric acid (Jayaprakasha and Sakariah, 2002). HCA is a potential anti-obesity agent (Heymsfield et al., 1998).

Garcinol, a polyisoprenylated benzophenone derivative, isolated from fruit rind of *Garcinia indica* has been traditionally used and appreciated for centuries. It has shown promising antioxidative, antiglycation, and free radical scavenging activities (Yamaguchi et al., 2000a,b). It has been reported that *garcinol* can play an important role in the treatment of gastric ulcers caused by the hydroxyl radicals or chronic infection with *Helicobacter pylori*. Presently, treatment with Clarithromycin antibiotic is the therapy of choice for treating *H. pylori* infection, which, however, suffers from emergence of rapid resistance (Chatterjee et al., 2003, 2005). Garcinol may be a viable alternative to Clarithromycin. Garcinol shows antibacterial activity comparable to that of the antibiotic Vancomycin against Methicillin-resistant *Staphylococcus aureus* (Rukachaisirikul et al., 2005). Garcinol is also effective at blocking the formation of azoxymethane-induced colonic aberrant crypt foci and induces apoptosis in human HL 60 cancer cells (Pan et al., 2001; Tanaka et al., 2000). Another study has further demonstrated that cigarette smoke extract-induced COX-2 expression is blocked by Garcinol pretreatment (Yang et al., 2009). Isogarcinol has also shown biological activities similar to that of garcinol and has been claimed to be an anti-inflammatory, antitumor, a lipase inhibitor, an antiobesity agent and an antiulcer agent (Sang et al., 2001).

* Corresponding author. Tel.: +91 9648029167; fax: +91 522 2342666.
E-mail address: chattsk@yahoo.com (S.K. Chattopadhyay).

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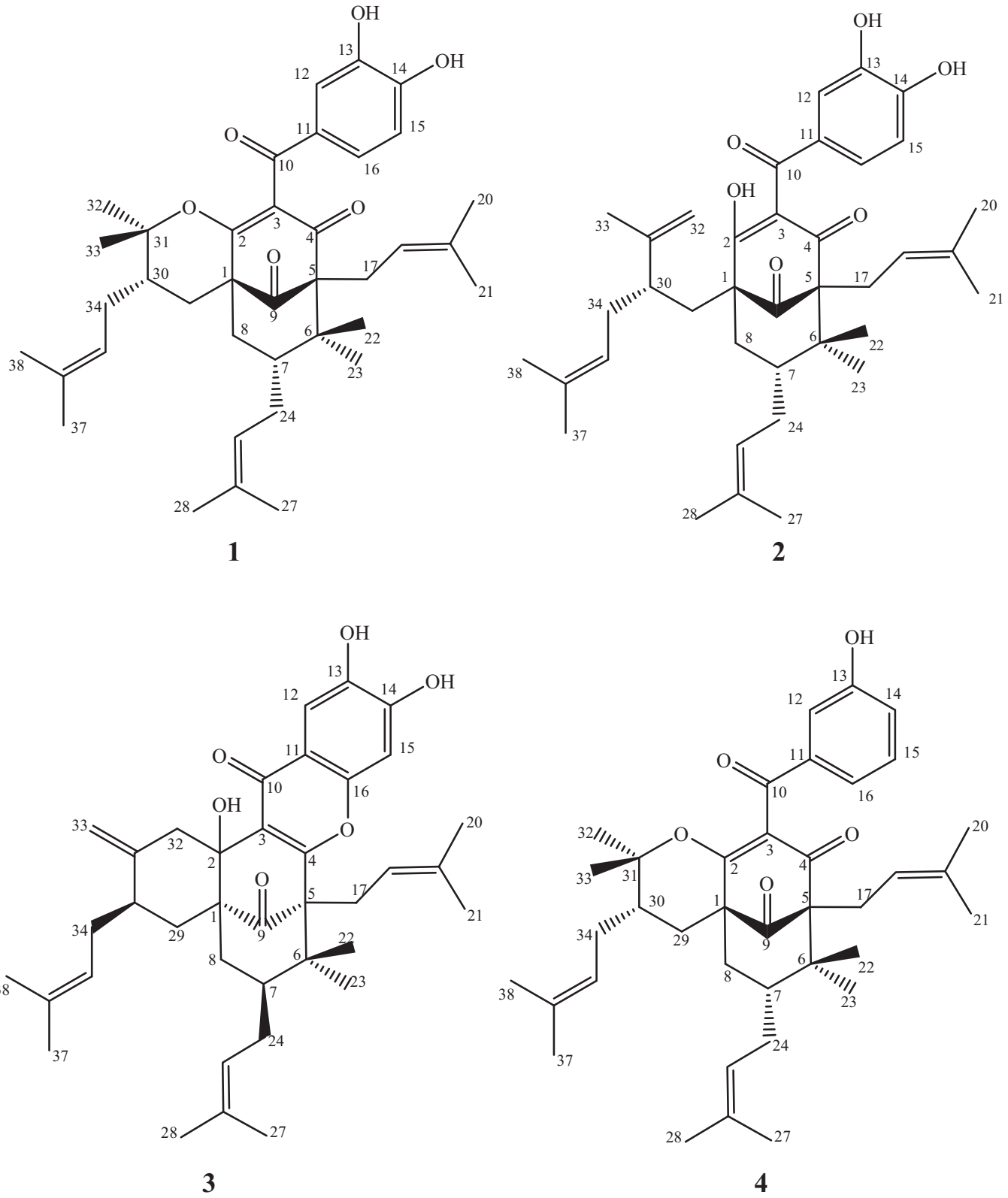


Fig. 1. Structures of compounds isolated from *Garcinia indica*.

As part of a study to characterize the biological activity of secondary metabolites from the fruits of *Garcinia indica*, we have previously isolated xanthochymol and isoxanthochymol from the fruits of *G. indica* and quantified their concentration in different parts of the plant by LC–MS/MS method (Kumar and Chattopadhyay, 2006). The objective of the present study was to develop a process technology for large scale extraction and isolation of isogarcinol (1) and garcinol (2) from kokam fruits. In order to study the detailed biological activities of isogarcinol (**1**) and garcinol (**2**), we have developed an upscaling process for isolation of

the two molecules in good quantities from 7 kg fruits of *G. indica*. During the upscaling process, we have also been able to isolate two other new minor compounds (**3**) and (**4**) (Fig. 1) from the fruits of *G. indica*. In this paper, we are reporting the large scale extraction and isolation process of isogarcinol (**1**) and garcinol (**2**) and structure elucidation of the two new molecules an acylphloroglucinol (**3**) and 14-deoxyisogarcinol derivatives (**4**) from the fruits of *Garcinia indica*.

2. Materials and methods

2.1. General

^{1}H and ^{13}C NMR spectra were recorded on a Bruker-Avance 400 MHz FT-NMR spectrometer operating at 400 and 100 MHz, respectively. The chemical shifts were expressed as δ (ppm, parts per million) referring to internal standard, tetramethylsilane (Me_4Si). ESI mass spectra was recorded on API 3000 triple quadrupole mass spectrometer (ABI-SCIEX, Toronto, Canada). HRMS data were acquired using electrospray ionization on an Agilent 6520 (Q-TOF) high resolution mass spectrometer. UV spectra were recorded on a Spectronic® GENESYS™ with a 10 mm quartz cell and IR spectra were recorded on a Perkin-Elmer Spectrum BX FT-IR spectrometer. Sample pellets were prepared in KBr using hydraulic pellet press of Kimaya manufacturers. Optical rotation was measured on Digipol 781 TDV (Rudolph Instrument) polrimeter. Silica Gel (60–120 mesh) and analytical TLC plates precoated with Si gel 60 F 254 were purchased from Merck (Mumbai-India). All other chemicals and solvents were of analytical grade and purchased from Loba Chemie (Mumbai, India).

2.2. Plant material

Fruit rinds of *Garcinia indica* were collected from Bengaluru. A herbarium sample was deposited in the gene bank of Central Institute of Medicinal and Aromatic Plants, Lucknow, India.

2.3. Large scale extraction and isolation of compounds from fruits G. indica

Air dried fruit rinds of *Garcinia indica* (7 kg) were cut in small pieces and grounded.

2.4. Stage 1: extraction with water, removal of hydroxycitric acid

Grounded plant material was suspended in water (6 × 5 L) for 24 h at 25 °C and filtered. The aqueous layer (22 L) so obtained was reduced to 8 L by membrane filtration technique. Aqueous layer obtained was defatted with hexane and freeze dried (1 kg). Aqueous layer contains Hydroxycitric acid as shown by HPLC analysis.

2.5. Stage 2: solid–matrix adsorption and sequential partitioning by different solvents

Marc left after water extraction was further extracted with methanol (6 × 5 L), methanolic extract (370 g) so obtained were pooled together, concentrated in vacuo at 40 °C and adsorbed with celite (1 kg). Adsorbed material was dried at 20–50 °C and extracted with hexane (5 × 2 L), chloroform (5 × 2 L), ethylacetate (5 × 2 L) successively. The extracts obtained by the above process were concentrated under vacuum at 40 °C to yield hexane extract (170 g), chloroform extract (32 g), ethyl acetate extract (15 g).

2.6. Purification of hexane extract

Hexane extract (170 g) was fractionated by silica gel column chromatography (10 cm × 150 cm, 2.0 kg), eluted with Petroleum ether–ethylacetate (100:0, 95:5, 90:10, 85:15, 80:20, 75:25, 60:40) to yield ten major fractions. Fraction 3 (0.5 g) was further purified by silica gel column chromatography (2 cm × 35 cm, 38 g) (eluted with petroleum ether–ethyl acetate 90:10) to yield compound **4**. Fraction 4 (35 g) was further purified by silica gel column chromatography (3 cm × 90 cm, 300 g) (eluted with petroleum ether-ethyl acetate 85:15) to yield compounds **1** (12 g), **2** (14 g) and **3** (400 mg).

2.7. Purification of chloroform extract

Chloroform extract (32 g) was subjected to silica gel column chromatography (3 cm × 90 cm, 300 g), eluted sequentially with petroleum ether, petroleum ether:ethyl acetate (85:15) and petroleum ether:ethyl acetate (50:50). About 50 fractions of 250 mL capacity were collected. The fractions obtained with petroleum ether–ethyl acetate 85:15 on further concentration and cooling down in refrigerator effectively precipitated out garcinol (3.2 g) and isogarcinol (1.5 g).

2.8. Purification of ethyl acetate extract

Ethylacetate extract (15 g) was subjected to silica gel column chromatography (3 cm × 90 cm, 150 g), eluted sequentially with petroleum ether, petroleum ether:ethyl acetate (85:15) and petroleum ether:ethyl acetate (50:50). About 50 fractions of 200 mL capacity were collected. The fractions obtained with petroleum ether–ethyl acetate 85:15 on further concentration and cooling down in refrigerator effectively precipitated out garcinol (1.2 g) and isogarcinol (1.8 g).

2.9. Spectroscopic data

2.9.1. Isogarcinol (*1*)

White powder; UV (MeOH) λ_{max} (log ε): 232(1.8), 277(2.0) nm; IR υ_{max}: 3367, 2920, 1720, 1620, 1590 cm^{-1}; the ^{1}H and ^{13}C NMR data are in agreement with those reported in the literature (Krishnamurthy et al., 1981, 1982; Rao et al., 1980; Rao and Venkatswamy, 1980; Sahu et al., 1989); ESI-MS *m/z* 601.6 $[M-H]^-$; $[\alpha]_D^{25}$ −269.8 (*c* 0.1, MeOH).

2.9.2. Garcinol (*2*)

Yellow powder; UV (MeOH) λ_{max} (log ε): 226(3.6), 271(4.0) nm; IR υ_{max}: 3300, 2920, 1720, 1640, 1590, 1457 cm^{-1}; the ^{1}H and ^{13}C NMR data are in agreement with those reported in literature (Krishnamurthy et al., 1981, 1982; Rao et al., 1980; Rao and Venkatswamy, 1980; Sahu et al., 1989); ESI-MS *m/z* 601.6 $[M-H]^-$; $[\alpha]_D^{25}$ −149.2 (*c* 0.1, MeOH).

2.9.3. Polyprenylated acylphloroglucinol derivative (*3*)

Yellow amorphous powder; UV (MeOH) λ_{max} (log ε): 295(2.1), 320(2.0) nm; IR υ_{max}: 3338, 1725, 1622, 1578, 1474 cm^{-1}; for ^{1}H and ^{13}C NMR spectroscopic data see Table 1. HR-ESI-MS *m/z* 601.3517 $[M+H]^+$ (calculated 601.3484); $[\alpha]_D^{25}$ +18.9 (*c* 0.1, MeOH).

2.9.4. 14-Deoxyisogarcinol (*4*)

White powder; UV (MeOH) λ_{max} (log ε): 205(3.8), 259(1.7) nm; IR υ_{max}: 3468, 3369, 1718, 1680, 1606, 1578, 1457 cm^{-1}; for ^{1}H and ^{13}C NMR spectroscopic data see Table 1. HR-ESI-MS *m/z* 587.3722 $[M+H]^+$ (calculated 587.3692); $[\alpha]_D^{25}$ −178.0 (*c* 0.1, MeOH).

Table 1
^{1}H and ^{13}C NMR spectroscopic data for compound **3** and **4** in $CDCl_3$.

Position	**3**		**4**	
	δ_H (J in Hz)	δ_C	δ_H (J in Hz)	δ_C
1		54.7		51.2
2		76.2		171
3		123.2		125
4		165.4		194
5		61.3		68.2
6		49.4		46.2
7	1.04 s	43.7	1.45 m	46.3
8	2.36 m	39.1	2.32 d(14.4)	39.8
	1.48 s		2.02 os	
9		210.2		207
10		178.5		193
11		116.1		138
12	7.64 s	107.9	7.35 bs	114.6
13		152.4		156.0
14		143.4	6.96 bs	120.7
15	6.93 s	102.6	7.17 m	121.4
16		151.5	7.17 m	129.3
17	2.63 m	27.3	2.66 m	25.5
	2.60 m		2.42 dd(13.4, 4.5)	
18	4.46 bs	118.7	4.91 bs	119
19		134.8		133.
20	1.38 s	25.8	1.59 s	26.0
21	1.60 s	18.0	1.58 s	18.0
22	0.99 s	20.0	0.98 s	26.7
23	1.04 s	25.1	1.16 s	22.4
24	2.32 m	31.2	2.67 m	29.2
	2.05 m		2.16 d(14.1)	
25	5.27 bs	122.8	4.91 bs	124.7
26		132.0		135
27	1.64 s	18.2	1.59 s	17.9
28	1.64 s	25.9	1.72 s	25.6
29	2.23 dd (13.2, 4.4)	36.7	3.07 dd (14.2, 3.7)	28.2
	1.25 s			
30	2.63 m	38.4	1.45 m	42.7
31		146.9		86.6
32	2.97 d(13.6)	47.2	1.25 s	21.1
	1.82 d (13.6)			
33	4.82 s	109.5	0.90 s	28.5
	4.87 s			
34	1.25 s	29.7	2.02 m	29.5
			1.72 os	
35	4.92 br s	122.5	5.12 bs	121.3
36		133.3		132.9
37	1.48 s	17.9	1.66 s	25.8
38	1.64 s	25.8	1.66 s	17.9

3. Result and discussion

Results of upscaling of garcinol and isogarcinol from 7 kg batch size are shown in Table 2. It is evident from the table that total yield of garcinol and isogarcinol is 0.48% of total dry weight of fruits. About 77% of the total garcinol and isogarcinol was isolated from the hexane extract.

3.1. Effect of application of solid matrix adsorption method

Liquid extraction technique in chemical process industries is applied to separate a component from a mixture of solvents by treatment with another solvent in which the desired component is preferentially more soluble. Although this process is commercially preferred but it requires selection of specific solvents having a good selectivity, recoverability, density difference, less viscosity and nondenaturing nature. Also in liquid extraction both of the phases have to be subjected to further mass transfer operations like distillation, crystallization, chromatography etc. for final recovery of the product. Sometimes formation of emulsions in fatty oil also complicates the process and making the process time consuming.

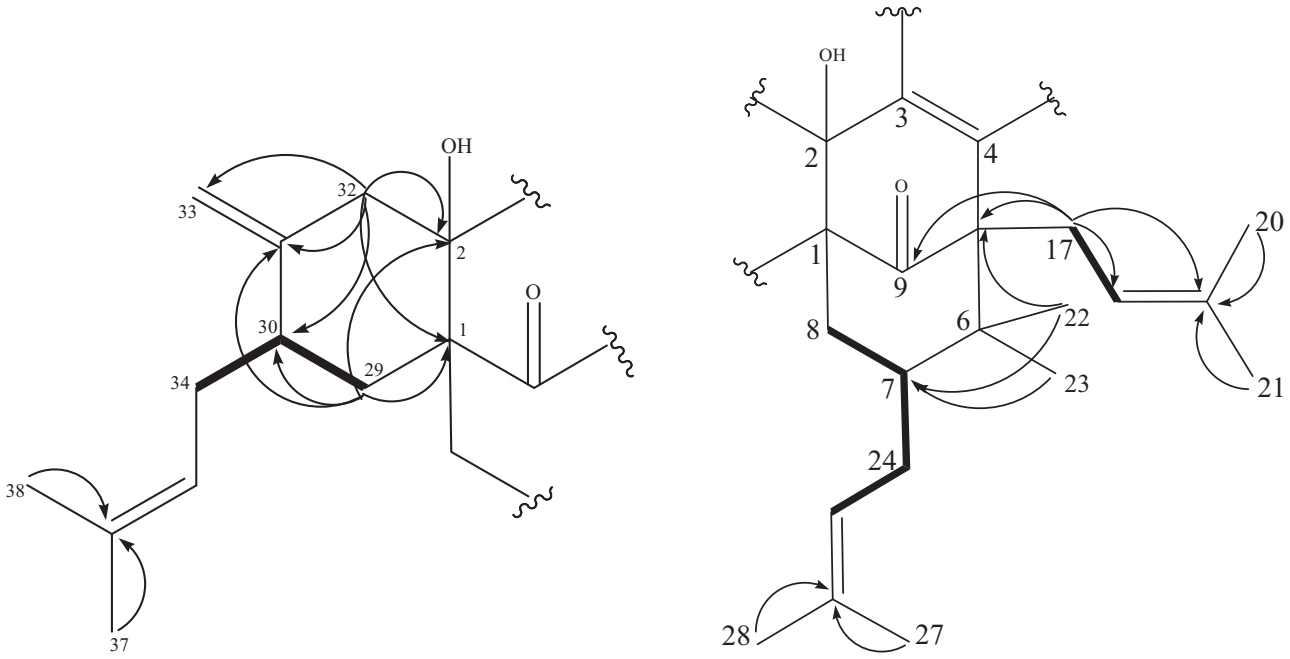
Due to the above difficulties, the application of solid matrix technique using a filtration aid was tried and was found to be best in terms of efficiency and economic. Also the process of dissolving crude extract in water and partitioning with various solvents is cumbersome and is not industrially feasible. The solid matrix technique involving an extract adsorbed to a solid matrix and partitioning with various solvents served a better option in terms of mass transfer and better extraction kinetics other than the conventional liquid–liquid partitioning.

3.2. Identification of compounds

The structures of isogarcinol (**1**) and garcinol (**2**) were established by comparison of their spectroscopic data with literature values (Krishnamurthy et al., 1981, 1982; Rao et al., 1980; Rao and Venkatswamy, 1980; Sahu et al., 1989). Compound **3** was obtained as a yellow amorphous solid, $[\alpha]_D^{25}$ +18.9 (*c* 0.1, MeOH) with a molecular formula of $C_{38}H_{48}O_6$ as determined by HR-ESI-MS at *m*/*z* 601.3517 $[M+H]^+$ (calculated 601.3484), suggesting 15° of unsaturation. The IR spectrum showed the presence of hydroxyl (3338 cm^{-1}), carbonyl (1725, 1622 cm^{-1}) and phenyl groups (1578, 1474 cm^{-1}). In accordance with the molecular formula, 38 carbon

Table 2
Column chromatography data of upscaling of garcinol and isogarcinol (batch size 7 kg).

Name of extract	Weight of extract (g)	Weight of garcinol isolated (g)	Weight of isoarcinol isolated (g)	Total yield of garcinol and isogarcinol (percent of dry fruit weight)
Hexane extract	170	14.0	12.0	0.37
Chloroform extract	32	3.2	1.5	0.07
Ethyl acetate extract	15	1.2	1.8	0.04
Total	217	18.4	15.3	0.48



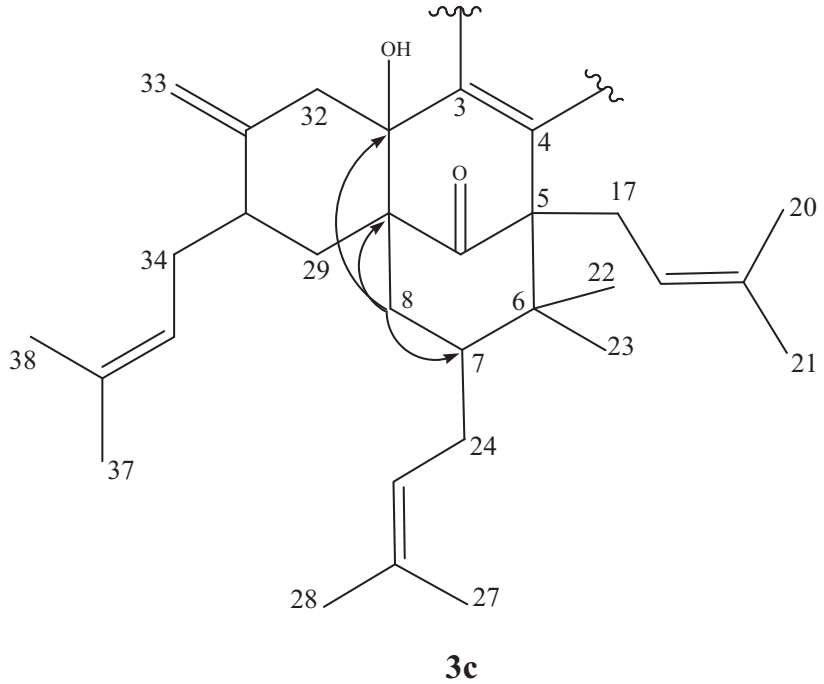


Fig. 2. Structural fragments, COSY (—) and HMBC (→) correlation of **3**.

resonances were resolved in the ^{13}C NMR spectrum, and were further classified by DEPT and HSQC experiments into the categories of 8 methyls, 7 methylenes (an olefinic carbon), 7 methines (including 3 olefinic and 2 aromatic carbons) and 16 quaternary carbons (including 4 phenyl, 2 carbonyls and 6 olefinic carbons). The 8 carbon–carbon double bonds and 2 carbonyl groups accounted for 10° of unsaturation, remaining 5° of unsaturation suggested that the molecule contained five rings.

Characteristic ^{13}C resonances including those of three oxygenated sp^2 carbons at δ_C 152.4 (C-13), δ_C 143.4 (C-14) and δ_C 151.5 (C-16) together with one sp^2 carbon atom at δ_C 116.1 (C-11) and two aromatic CH singlets at δ_H 6.93 and 7.64 indicated the presence of a 1,2,4-trioxygenated benzene ring. Downfield shift of the aromatic proton at δ_H 7.64 suggested it to be β to carbonyl group which was assigned as γ pyrone functionality due to its IR absorption (1622 cm^{-1}) and ^{13}C resonance (δ_C 178.5) respectively.

Resonance for 6 membered ring containing an isolated carbonyl group (δ_C 210.2, C-9) flanked between two quaternary carbons (δ_C 54.7, C-1; δ_C 61.3, C-5) and an enolizable 1, 3 dioxygenated carbons (δ_C 76.2, C-2; δ_C 123.2, C-3 and δ_C 165.4, C-4) were also observed. Support for this assignment was provided by ^{13}C NMR signals for quaternary (δ_C 49.4, C-6), methine (δ_C 43.7, C-7) and methylene (δ_C 39.1, C-8) carbon which were a part of [3.3.1] nonane ring system. The ^1H NMR spectrum indicated for the presence of 3 trisubstituted olefinic protons [δ_H 4.46 (1H, s); 4.92 (1H, br s); 5.27 (1 H, s)], one terminal olefine [δ_H 4.85 (2H, d, J = 10.4 Hz)], 8 methyl groups out of which 6 were attached to olefinic carbons and remaining two were present as geminal dimethyl groups [δ_H 0.99 (3H, s), δ_C 20.0 and δ_H 1.04 (3H, s), δ_C 25.1] attached to a quaternary carbon at δ_C 49.4 (C-6). Three olefinic protons along with six methyl groups attached to olefinic carbons indicated them to be a part of three isoprene side chains.

In addition, the presence of a six membered ring consisting of one oxygenated sp^3 carbon (δ_C 76.2, C-2), one quaternary carbon (δ_C 54.7, C-1), two methylene carbons [δ_H 1.82 (1H, d, J = 13.6 Hz), δ_H 2.97 (1H, d, J = 13.6 Hz), δ_C 47.2, C-32] [δ_H 2.23 (1H, d, J = 13.2, 4.4 Hz), 1.25 (1H, s); δ_C 36.7, C-29], one methine carbon [δ_H 2.63 (1H, m), δ_C 38.4, C-30] along with one olefinic quaternary carbon at δ_C 146.9 (C-31) were observed.

Partial structure obtained so far was further refined with the help of HMBC, COSY and NOESY data. HMBC correlation between (a) H_2-29 (δ_H 2.23, 1.25) and C-30 (δ_C 38.4), C-31 (δ_C 146.9), C-2 (δ_C 76.2) and C-1 (δ_C 54.7); (b) H_2-32 (δ_H 1.82, 2.97) and C-30 (δ_C 38.4), C-33 (δ_C 109.5), C-31 (146.9), C-2 (δ_C 76.2) and C-1 (δ_C 54.7) along with COSY correlation between H_2-34, H_1-30 and H_2-29 further confirmed that compound **3** has a cyclohexyl ring with one exocyclic double bond at C-31 and an isoprenyl group attached to the C-30. This has further confirmed **3a** (Fig. 2) to be a part of compound **3**.

In addition the HMBC spectrum of **3** also showed correlation from H_3-22 (δ_H 0.99) to C-5 (δ_C 61.3); from H_3-23 (δ_H 1.04) to C-7 (δ_C 43.7), C-5 (δ_C 61.3); from H_2-17 (δ_H 2.63, 2.60) to C-5 (δ_C 61.3), C-9 (δ_C 210.2), C-18 (δ_C 118.7) and C-19 (δ_C 134.8). The observed HMBC correlation showed that **3** has a bicyclo [3.3.1] nonane ring system with two isoprene units attached at C-5 and C-7 respectively and geminal dimethyl groups attached at C-6, which led to partial structure **3b** (Fig. 2). Further HMBC correlation from H_2-8 (δ_H 2.36, 1.48) to C-1 (δ_C 54.7), C-2 (δ_C 76.2), and C-7 (δ_C 43.7) permitted us to join the two fragments **3a** and **3b** as shown in Fig. 2.

The relative configuration of **3** was confirmed on the basis of NOE experiment (Fig. 3). For polyisoprenylated benzophenone, Grossman and Ciochina (2006) have recommended that the conformation of saturated ring (chair or boat) and the orientation of C-7 prenyl group (exo or endo) can be established on the bases of NMR chemical shift analysis for the ring CH_2-8 (^1H), geminal

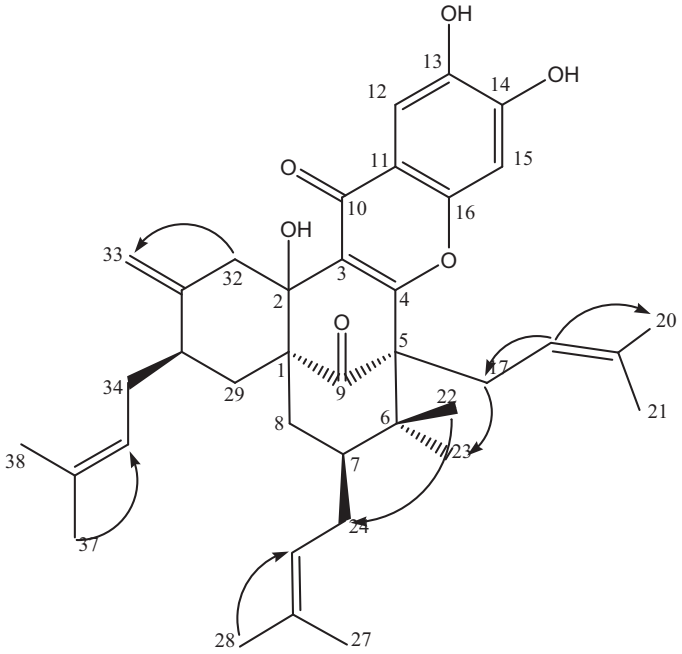


Fig. 3. Key NOESY (→) correlation of **3**.

methyls (^{13}C), and C-7 (^{13}C). With a chair conformation and an exo C-7 prenyl, the following values are usually found: $\Delta\delta_H$ ca. 0.5 ppm (ring CH_2-8), $\Delta\delta_C$ ca. 7.7 ppm (geminal methyls), and the C-7 chemical shift at δ_C 43 ppm. In contrast, with a boat conformation and endo C-7 prenyl, the values would be $\Delta\delta_H$ ca. 0.2 ppm (ring CH_2-8), $\Delta\delta_C$ ca. 4.0 ppm (geminal methyls), and the C-7 chemical shift at δ_C 48 ppm. For compound **3**, the diastereotopic ring CH_2-8 proton signals resonated 0.883 ppm apart, the diastereotopic Me groups (Me-22 and Me-23) resonated 5.05 ppm apart, and the C-7 chemical shift was found at δ_C 43.7 ppm. Thus, the structure **3** was deduced to have chair conformation in the more saturated ring (C-1, C-5, C-6, C-7, C-8 and C-9) with an exo C-7 prenyl group.

By further NOESY correlation between H_3-23 and H_2-17 it was confirmed that these were in equatorial orientation whereas correlation between H_3-22 and H_2-24 suggested them to be in axial orientation (Fig. 3). The polycyclic prenylated acylphloroglucinols for which absolute configurations have been determined experimentally are xanthochymol, guttiferone E, and garcinol. Certain compounds, however, have been isolated in both enantiomeric forms. In this regard, some authors have suggested that the specific rotation (positive or negative) of a compound can reveal its absolute configuration. However, caution should be exercised because of the possibility of the presence of impurities at high optical rotation and also because comparing the optical rotation of a natural product to that of a chemically related molecule can be unreliable and should not be assumed to be definitive (Huang et al., 2009; Stephens et al., 2008). Therefore, the absolute configurations for **3** remain undetermined in the present study.

Compound **4** was obtained as a white powder. Its HR-ESI-MS exhibited a molecular ion peak at m/z 587.3722 $[M+H]^+$ (calculated 587.3692) corresponding to molecular formula of $C_{38}H_{50}O_5$ with 14° of unsaturation The IR spectrum showed the presence of hydroxyl (3468, 3369 cm^{-1}), carbonyl (1718, 1680, 1606 cm^{-1}) and phenyl groups (1578, 1457 cm^{-1}). Initial observation of the ^{13}C NMR and DEPT spectrum of **4** found 38 signals, assigned as three carbonyls, six phenyl carbons, eight olefinic carbons, five methylene carbons and two sp^3 methine carbons. Both 1D and 2D NMR spectra of **4** showed close similarity with spectrum of Isogarcinol **1** except in the aromatic region.

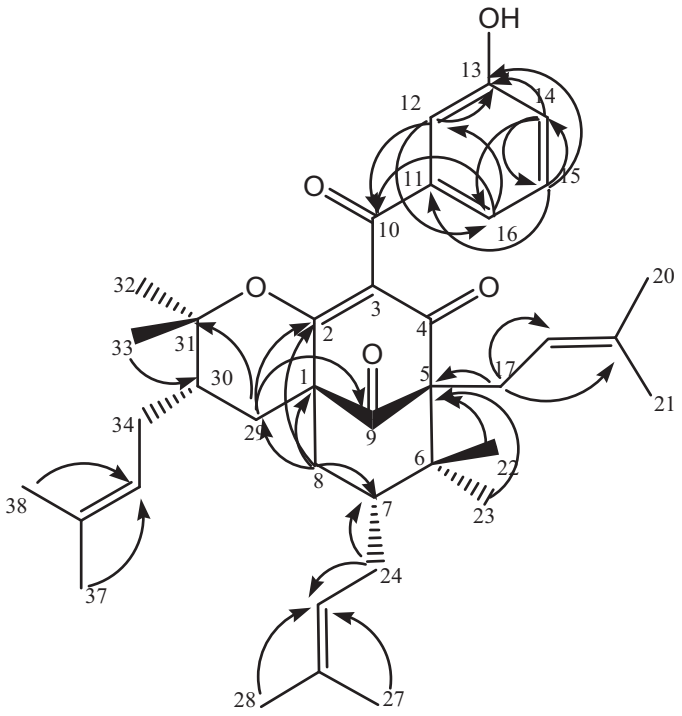


Fig. 4. Key HMBC (→) correlation of **4**.

^{1}H NMR of **4** has showed 3 aromatic signals at δ_H 6.96, 7.17 and 7.35 respectively integrating for four protons, that was in contrast with isogarcinol which has only 3 aromatic protons. Characteristic ^{13}C signals including four sp^2 CH at δ_C 114.6, 120.7, 121.4 and 129.3 along with one oxygenated sp^2 carbon at δ_C 156 and one sp^2 carbon at δ_C 138 indicated the presence of 1,3-disubstituted benzene ring. This was further confirmed by HMBC correlation (Fig. 4) that 3-hydroxy benzoyl group replaced the 3,4-dihydroxy benzoyl group present in isogarcinol (**1**).

Comparison of the NMR data with those of Isogarcinol (**1**) led to the conclusion that the structure **4** is closely comparable to that of Isogarcinol, except for the 3-hydroxybenzoyl group. All these assignments were further confirmed by the analysis of HSQC, HMBC, COSY and NOESY NMR experiments. HMBC correlation from H-14 (δ_H 6.96) to C-13 (δ_C 156.0), C-15 (δ_C 121.4), C-16 (δ_C 129.3); from H-15 (δ_H 7.17) to C-13 (δ_C 156.0), C-14 (δ_C 120.7), C-11 (δ_C 138.0); from H-16 (δ_H 7.17) to C-12 (δ_C 114.6), C-10 (δ_C 193.0), C-14 (δ_C 120.7) and from H-12 (δ_H 7.35) to C-13 (δ_C 156.), C-16 (δ_C 129.3), C-10 (δ_C 193.0) further confirmed the presence of 1,3-disubstituted benzene ring. Analogy of optical rotation of **4** $[\alpha]_D^{25}$ −178.0 (*c* 0.1, MeOH) with isogarcinol $[\alpha]_D^{25}$ −269.8 (*c* 0.1, MeOH) was also observed. Accordingly the structure **4** was assigned to 14-deoxyisogarcinol.

4. Conclusion

Due to significant biological importance of garcinol and isogarcinol, we have developed a process technology for the large scale extraction and isolation of these molecules from fruits of *Garcinia indica*. The process technology described in this paper would be helpful in large scale isolation of these molecules from the fruits of *G. indica*, would provide new opportunities to further explore the biology of these molecules. This study also afforded two new polyprenylated benzophenone compounds isolated for the first time from the fruits of *Garcinia indica*. The structures of the two new molecules were established unambiguously by extensive spectral analysis.

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