

GARCINOL, A NOVEL ARYLBENZOFURAN DERIVATIVE FROM
GARCINIA KOLA

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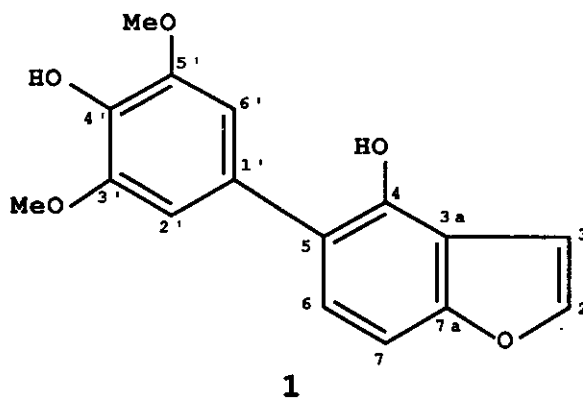
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Abstract ----- A novel arylbenzofuran named garcinol was isolated from *Garcinia kola* Heckel (Guttiferae) collected in Nigeria and the structure was elucidated by spectroscopic methods.

The plants of garcinia genus (Guttiferae) are known as a toxic plant and some of them are used as a traditional herb medicine in the areas of southeastern Asia.¹ But the chemical constituents are little studied. In the course of phytochemical studies of medicinal plants, we isolated a novel arylbenzofuran derivative named garcinol from roots of *Garcinia kola* Heckel (Guttiferae) collected in Nigeria. In this paper, we wish to describe the isolation and structure of garcinol (1).

The ethanol extract was subjected to medium pressure chromatography on silica gel using a mixture of chloroform and methanol (20 : 1) to give garcinol (1) as colorless liquid : C₁₆H₁₄O₅ [*m/z* 286.0848; calcd 286.0840]; uv (MeOH) λ 218 (ε 26600), 245 (ε 19800), 250 sh. (ε 14800), 268 sh. (ε 7700) nm; ir (film) ν 3400 br. cm⁻¹; δ_H (CD₃OD) 3.86 (6H, s), 6.80 (2H, s, H-2', H-6'), 6.96 (1H, dd, J=2.2, 0.7 Hz, H-3), 7.04 (1H, dd, J=8.4, 0.7 Hz, H-7), 7.17 (1H, d, J=8.4 Hz, H-6), 7.62 (1H, d, J=2.2 Hz, H-2) ppm; δ_C (CD₃OD) 57.6 (OMe x 2), 105.0 (C-7), 105.9 (C-3), 109.2 (C-2', C-6'), 119.6 (C-3a), 124.5 (C-5), 129.0 (C-6), 131.9 (C-1'), 136.4 (C-4'), 145.8 (C-2), 149.0 (C-4), 149.8 (C-3', C-5'), 157.9 (C-7a) ppm.

In the ^1H -nmr spectrum of **1**, two AB-type signals were observed. One pair (δ_{H} 7.04 and 7.17 ppm) having $J=8.4$ Hz was assigned to *ortho*-located aromatic protons on a benzene ring and the remaining pair (δ_{H} 6.96 and 7.62 ppm) having $J=2.2$ Hz to *vicinal*-located protons on a furan ring. The small coupling constant ($J=0.7$ Hz) between a proton at δ_{H} 6.96 ppm and a proton at δ_{H} 7.04 ppm suggested the characteristic long range coupling between the 3- and 7-protons in a benzofuran.² Namely, garcinol was proposed to be 4,5-disubstituted benzofuran. Two substituent groups and their locations were determined as follows. The nmr data (δ_{H} 3.86 (6H, s) and 6.80 ppm (2H, s), and δ_{C} 57.6, 109.2 and 149.8 ppm) suggested the presence of a symmetrical partial structure; 3,5-dimethoxy-4-hydroxyphenyl group or 2,6-dimethoxy-4-hydroxyphenyl group. The adoption of and the location (C-5) of the former group were determined by HMBC experiment.³ These were furthermore supported by NOE experiment. 22.5% enhancement of the signal at δ_{H} 6.80 (H-2' (6')) was observed by irradiation of the signal at δ_{H} 3.86 (OMe). On irradiation of the signal at δ_{H} 6.80, 19.2 and 5.0% enhancements of the signals at δ_{H} 3.86 and at δ_{H} 7.17 (H-6), respectively were observed. Consequently, the remaining substituent was a hydroxy group which was located at C-4 of the benzofuran.⁴ This conclusion was also supported by close resemblance of the δ_{H} values of protons on the benzofuran ring between garcinol and 2'-hydroxy-4-methoxyfurano(3',4'-4'',5'')chalcone [δ_{H} 7.02 (dd, $J=2.2, 0.8$ Hz), 7.08 (dd, $J=8.9, 0.8$ Hz), 7.58 (d, $J=2.2$ Hz), and 7.86 (d, $J=8.9$ Hz)].⁴



Thus, the structure of garcinol should be 4-hydroxy-5-(3',5'-dimethoxy-4'-hydroxyphenyl)benzofuran (1).

Garcinol (1) is the first example of natural 5-arylbenzofuran.

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REFERENCES AND NOTE

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3. In HMBC experiment, cross peaks were observed between H-2 and C-3, H-2 and C-3a, H-2 and C-7a, H-3 and C-2, H-3 and C-3a, H-3 and C-7a, H-6 and C-4, H-6 and C-5, H-6 and C-7a, H-7 and C-3a, H-7 and C-5, H-2' (6') and C-5, H-2' (6') and C-3' (5'), and H-2' (6') and C-4', respectively.
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