GARCINOL, A NOVEL ARYLBENZOFURAN DERIVATIVE FROM *GARCINIA KOLA*

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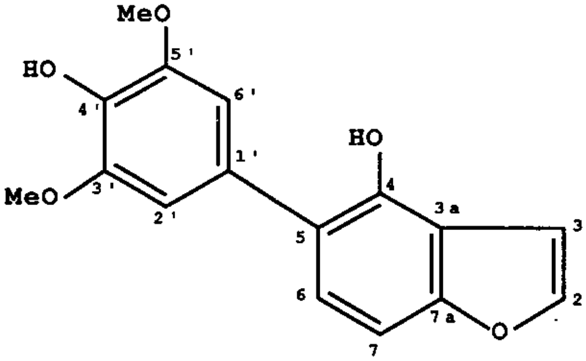
Abstract ----- A novel arylbenzofuran named garcinol was isolated from *Garcinia kola* Heckel (Guttiferae) collected in Nigeria and the structure was elucidated by spectroscopic methods.

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 : $C_{16}H_{14}O_5$ [*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 (CD_3OD) 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 (CD_3OD) 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 ^{1}H-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]



1

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.

ACKNOWLEDGEMENT

We are grateful to Dr. C. Itoh, Meijo University for the HMBC measurement, and also grateful to Dr. S. Kosemura, Keio University for valuable discussion.

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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Received, 12th November, 1992