Asian Journal of Chemistry; Vol. 25, No. 17 (2013), 9481-9484

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.15031

GC-MS Analysis of Liposoluble Constituents of Different Parts of *Dimocarpus longan*

XIAOWEI ZHANG, WEI CAO*, YUKUN WANG, LI CUN and SIWANG WANG*

Department of Natural Medicine, School of Pharmacy, Fourth Military Medical University, Xi'an 710032, P.R. China

*Corresponding author: Fax: +86 29 83224790; Tel: +86 29 84773752; E-mail: caowei@fmmu.edu.cn, siwangw@fmmu.edu.cn

(*Received*: 26 December 2012; *Accepted*: 1 October 2013) AJC-14210

The liposoluble constituents from the aril, husk and kernel of longan were studied. The gas chromatography-mass spectrometry (GC-MS) and computer spectrum searching technique were applied. 15, 34 and 33 compounds were identified from the petroleum ether extracts of the aril, husk and kernel of longan respectively. The study on the liposoluble constituents of the aril, husk and kernel of longan provided the test basis for the further development and utilization of Dimocarpus Longan Lour resources.

Key Words: Longan, GC-MS, Liposoluble constituents.

INTRODUCTION

Longan (*Dimocarpus longan* Lour.), which originated from Southeast Asia, is a non-climacteric subtropical fruit of the Sapindaceae family[1]. It is widely accepted by consumers and has established great popularity in the international market with strong demand for the desirable flavor and health benefits[2,3]. The flesh (aril) of the fruit is served for stomachic, febrifuge and vermifuge, as well as antidote in clinic. Decoction of the dried flesh is also taken as a tonic or alternative treatment for insomnia and neurasthenic neurosis. In addition, longan kernel has also been used in traditional Chinese medicine for the treatment of cardiovascular and immunological diseases, such as tonifying both the heart and spleen and increasing the immunomodulatory capacity[4]. In recent years, the extracts of longan fruit such as aril, husk and kernel, has exhibited excellent antioxidant, anti-tyrosinase and antitumor activities[5-12].

Longan fruit is rich in carbohydrates, protein, fiber, fat, vitamin C, amino acids and minerals. Previous studies have identified phenolic compounds including gallic acid, corilagin, ellagic acid and their conjugates, (-)-epicatechin, 4-*o*-methyl gallic acid, flavone glycosides, glycosides of quercetin and kaempferol from longan husk[13-16] and ethyl gallate 1-β-*o*-galloyl-D-glucopyranose, methyl brevifolin carboxylate, grevifolinand 4-*o*-α-L-rhamnopyranosyl-ellagic acid, gallic acid, corilagin and ellagic acid from longan kernel[17]. Longan aril contains lysophosphatidyl choline, phosphatidyl choline, phosphatidyl inositol, phosphatidyl serine, phosphatidyl ethanolamine, phosphatidate and phosphatidic acid glycerol[18]. Such phospholipids can be metabolized by a variety of membrane lipid-related enzymes and may improve immune function. In addition, longan husk contains significant amounts of polysaccharides[19].

Although many studies have shown nutritional and phytochemical compositions of longan, there is little information on the liposoluble components. The purpose of this study was to identify the liposoluble compounds of different parts of the longan by GC-MS.

EXPERIMENTAL

Dried longan fruits (*D. longan* Lour.) were harvested in Putian, Fujian, China. The fruits were manually separated into the aril, husk and kernel. Then they were dried by oven and finally pulverized into powder by a mill. The materials were stored in a desiccator at room temperature until use[20].

Sample preparation: Longan aril powder (2.44 kg), husk powder (3.00 kg) and kernel powder (4.92 kg) were immersed, respectively in 95 % ethanol and refluxed for 3 times, 3 h each time. Then the extracts were combined, filtered while hot and evaporated on a vacuum concentrator system. After the extractions were extracted with petroleum ether, longan aril extract (14.5 g), husk extract (31.1 g) and kernel extract (114.8 g) were obtained.

GC-MS conditions: Liposoluble constituents were analyzed by a Shimadzu GC-MS-QP2010PLUS apparatus under the conditions shown in Table-4[21]. Compounds were identified using the National Institute of Standards and Technology (NIST) MS spectral database and Kovats index.

RESULTS AND DISCUSSION

The analysis results of aril, husk and kernel of longan were given in Tables 1-3, respectively. Fifteen compounds were

TABLE-1
LIPOSOLUBLE COMPOUNDS IDENTIFIED IN ARIL OF LONGAN BY GC-MS

No.	R.T (min)	Compounds	Formula	m.w.	Amount (%)
1	13.45	5-(Morpholino)pent-2-en-4-ynal	$C_9H_{11}NO_2$	165	2.00
2	13.73	Cyclononanone	$C_9H_{16}O$	140	1.29
3	15.16	Di-isobutyl phthalate	$C_{16}H_{22}O_4$	278	10.78
4	15.50	Hexadecanoic acid	$C_{16}H_{32}O_2$	256	11.22
5	15.72	Ethyl palmitate	$C_{18}H_{36}O_2$	284	6.56
6	15.84	1-Docosene	$C_{22}H_{44}$	308	0.60
7	15.92	Heneicosane	$C_{21}H_{44}$	296	0.52
8	17.19	Oleic acid	$C_{18}H_{34}O_2$	282	10.66
9	17.37	Ethyl oleate	$C_{20}H_{38}O_2$	310	10.31
10	17.65	Squalene	$C_{30}H_{50}$	410	17.96
11	20.51	Di-*n*-octyl phthalate	$C_{24}H_{38}O_4$	390	0.86
12	21.19	Nonacosane	$C_{29}H_{60}$	408	0.70
13	22.55	Heptadecanoic acid,ethyl ester	$C_{19}H_{38}O_2$	298	1.31
14	23.40	Tetracontane	$C_{40}H_{82}$	563	0.40
15	27.55	8'-Apo-β-caroten-8'-al	$C_{30}H_{40}O$	416	1.67

TABLE-2
LIPOSOLUBLE COMPOUNDS IDENTIFIED IN HUSK OF LONGAN BY GC-MS

No.	R.T (min)	Compounds	Formula	MW	Amount (%)
1	15.84	6,10,14-Trimethyl-2-pentadecanone	$C_{18}H_{36}O$	268	0.25
2	17.27	*n*-Nonadecane	$C_{19}H_{40}$	268	0.26
3	17.62	Di-isobutyl phthalate	$C_{16}H_{22}O_4$	278	2.41
4	18.48	Hexadecanoic acid	$C_{16}H_{32}O_2$	256	12.70
5	18.84	Ethyl palmitate	$C_{18}H_{36}O_2$	284	2.49
6	19.23	Heneicosane	$C_{21}H_{44}$	296	0.47
7	21.55	9,12-Octadecadienoic acid	$C_{18}H_{32}O_2$	280	4.90
8	21.61	*cis*-3-Butyl-4-vinyl-cyclopentene	$C_{11}H_{18}$	150	2.99
9	21.69	Octadec-9-enoic acid	$C_{18}H_{34}O_2$	282	6.66
10	21.83	Ethyl linoleate	$C_{20}H_{36}O_2$	308	3.19
11	21.90	Lionlenic acid, ethyl ester	$C_{20}H_{34}O_2$	306	1.42
12	22.00	Ethyl oleate	$C_{20}H_{38}O_2$	310	1.73
13	24.99	Octadecanoic acid, 5-hydroxy-,delta-lactone	$C_{18}H_{34}O_2$	282	1.21
14	26.00	Ethyl ester of Elcosanoic acid	$C_{22}H_{44}O_2$	340	0.25
15	27.25	Octadecanoic acid,3-oxo-,methyl ester	$C_{19}H_{36}O_3$	312	0.34
16	28.03	1,2-Benzenedicarboxylic acid,*bis*(2-ethylhexyl)ester	$C_{24}H_{38}O_4$	390	0.74
17	28.85	Ethyl 9-hexadecenoate	$C_{18}H_{34}O_2$	282	0.36
18	29.19	Heptadecanoic acid, ethyl ester	$C_{19}H_{38}O_2$	298	1.33
19	29.48	Hexacosane	$C_{26}H_{54}$	366	0.31
20	32.55	Squalene	$C_{30}H_{50}$	410	5.71
21	34.92	3.beta.-Acetoxystigmasta-4,6,22-triene	$C_{31}H_{48}O_2$	452	0.84
22	35.40	(2S)-2,5,7,8-Tetramethyl-2-[(4S,8S)-4,8,12-trimethyltridecyl]-3,4-dihydro-2*H*-chromen-6-ol	$C_{28}H_{48}O_2$	416	0.89
23	35.70	Cholesta-4,6-diene-3β-ol	$C_{27}H_{44}O$	384	2.65
24	35.99	Stigmast-5-en-3-ol,oleate	$C_{47}H_{82}O_2$	679	0.46
25	36.46	Heptacosane,1-chloro-	$C_{27}H_{55}Cl$	414	0.48
26	37.57	Campesterol	$C_{28}H_{48}O$	400	1.76
27	37.75	2,2,4A,6A,8A,9,12B,14A-Octamethyl-1,2,3,4,4A,5,6,6A,6B,7,8,8A,9,12,12A,12B,13,14	$C_{30}H_{50}$	410	0.72
28	37.99	Stigmasterol	$C_{29}H_{48}O$	412	4.11
29	38.78	γ-Sitosterol	$C_{29}H_{50}O$	414	12.16
30	39.10	4,4,6A,6B,8A,11,11,14B-Octamethyl-1,4,4a,5,6,6A,6B,7,8,8A,9,10,11,12, 12A,14,14A	$C_{30}H_{48}O$	424	1.14
31	39.70	Methyl commated	$C_{31}H_{50}O_4$	486	0.95
32	39.96	Cholesta-3,5-dien-7-one	$C_{27}H_{42}O$	382	0.61
33	41.40	Friedelinol	$C_{30}H_{52}O$	428	2.76
34	41.77	Friedelan-3-one	$C_{30}H_{50}O$	426	10.82

identified from the petroleum ether extract of the aril of longan, occupying 76.84 % of the total extracts. The main compositions were squalene (17.96 %), hexadecanoic acid (11.22 %), di-isobutyl phthalate (10.78 %), oleic acid (10.66 %), ethyl oleate (10.31 %) and ethyl palmitate (6.56 %). Thirty four compounds were identified from the petroleum ether extract of the husk of longan, occupying 90.07 % of the total extracts. The main compositions were γ-sitosterol (12.16 %), hexadecanoic acid (12.70 %), friedelinol (10.82 %), 9,12-octadecadienoic acid (4.90 %), (Z,Z)-octadec-9-enoic acid (6.66 %), squalene (5.71 %), stigmasterol (4.11 %). Thirty three compounds were identified from the petroleum ether extract of the kernel of longan, occupying 89.05 % of the total extracts. The main compositions were hexadecanoic acid (21.28 %), oleic acid

TABLE-3
LIPOSOLUBLE COMPOUNDS IDENTIFIED IN KERNEL OF LONGAN BY GC-MS

No.	R.T (min)	Compounds	Formula	m.w.	Amount (%)
1	17.71	Di-isobutyl phthalate	$C_{16}H_{22}O_4$	278	0.29
2	19.44	Hexadecanoic acid, methyl ester	$C_{17}H_{34}O_2$	270	0.14
3	20.55	Hexadecanoic acid	$C_{16}H_{32}O_2$	256	21.28
4	20.81	Ethyl palmitate	$C_{18}H_{36}O_2$	284	3.05
5	22.73	9-Octadecenoic acid(Z)-,methyl ester	$C_{19}H_{36}O_2$	296	0.11
6	23.10	Heneicosane	$C_{21}H_{44}$	296	0.12
7	23.80	Oleic acid	$C_{18}H_{34}O_2$	282	42.13
8	24.00	Ethyl oleate	$C_{20}H_{38}O_2$	310	4.40
9	24.55	Octadecanoic acid,ethylester	$C_{20}H_{40}O_2$	312	0.68
10	25.96	Ethyl 9-hexadecenoate	$C_{18}H_{34}O_2$	282	1.28
11	28.00	Ethyl ester of elcosanoic acid	$C_{22}H_{44}O_2$	340	0.27
12	29.25	1,3,5-Trisilacyclohexane	$C_3H_{12}Si_3$	132	0.41
13	30.03	1,2-Benzenedicarboxylic acid,*bis*(2-ethylhexyl)ester	$C_{24}H_{38}O_4$	390	0.18
14	31.82	1,1-dichloro-2,2,3,3-tetramethylcyclopropane	$C_7H_{12}Cl_2$	166	0.18
15	31.93	Heptanoic acid,docosul ester	$C_{29}H_{58}O_2$	438	1.00
16	32.16	2-phenylethyl dodecanoate	$C_{20}H_{32}O_2$	304	0.43
17	32.48	3-hydroxy-2-methyl-4-pyrone	$C_6H_6O_3$	126	0.55
18	32.97	Tetratetracontane	$C_{44}H_{90}$	619	0.17
19	34.15	Heptadecanoic acid ethyl ester grade I	$C_{19}H_{38}O_2$	298	0.15
20	34.41	Hexacosane	$C_{26}H_{54}$	366	0.13
21	34.54	Squalene	$C_{30}H_{50}$	410	0.66
22	34.75	Benzol,1,2-*bis*(9-borabicyclo[3.3.1]non-9-yloxymethyl)-	$C_{24}H_{36}B_2O_2$	378	0.51
23	35.05	4-Hydroxyphenyl 4-Butylcyclohexanecarboxylate	$C_{17}H_{24}O_3$	276	0.48
24	36.38	Dodecanoic acid,2-Phenylethyl ester	$C_{20}H_{32}O_2$	304	0.18
25	36.65	4-Hydroxyphenyl 4-Butylcyclohexanecarboxylate	$C_{17}H_{24}O_3$	276	0.22
26	37.98	Cholest-5-en-3-ol(3.beta)-,propanoate	$C_{30}H_{50}O_2$	442	0.32
27	38.44	Vitamin E	$C_{29}H_{50}O_2$	430	0.37
28	38.56	11-(2,5-Dimethylcyclohexyl)heneicosane	$C_{29}H_{58}$	406	0.48
29	38.90	Glycerine-1-oleate-3-palmitate	$C_{37}H_{70}O_5$	595	3.03
30	39.56	Ergost-5-en-3-ol,(3.bate.)-	$C_{28}H_{48}O$	400	0.61
31	39.98	Stigmasterol	$C_{29}H_{48}O$	412	1.62
32	40.75	γ-Sitosterol	$C_{29}H_{50}O$	414	3.13
33	41.69	9,19-Cyclolanost-23-ene-3,25-diol,3-acetate,(3.bate.,23E)-	$C_{32}H_{52}O_3$	484	0.49

TABLE-4
SELECTED PARAMETERS FOR GC-MS DETERMINATION

Parameter	Description
Injection method	Splitless mode (0.5 min)
Injection volume	1 µL
Injector temperature	270 ºC
Split ratio	50:1
Capillary column	DB-5MS(30 m × 0.32 mm, 0.25 µm)
Carrier gas	Nitrogen
Flow rate	1.91(aril), 2.10(husk, kernel)mL/min (constant flow)
Temperature program	Aril: Initial 50 ºC (7min) programmed at 20 ºC/min to 80 ºC, (2 min), at 10 ºC/min to 290 ºC (5 min) Husk: Initial 50 ºC (7min) programmed at 20 ºC/min to1 80 ºC, (13min), at 5 ºC/min to 290 ºC (6 min) Kernel: Initial 50 ºC (7min) programmed at 20 ºC/min to 100 ºC, (2 min), at 10 ºC/min to 290 ºC (6min)
Mass spectrometer temperature	200 ºC
Ionization	EI mode at 70 eV
Analysis mode	Full scan, two scans per second mass range, 20-800 m/z

(42.13 %) and ethyl oleate (4.40 %). The main types of these compounds were organic acid, sterol, alkene, esters, alkane, ketone, unsaturated fatty acid, *etc*.

In the present study, present results indicated that squalene was the main compound of the liposoluble constituents of longan aril. Squalene is found throughout nature in plant and animal sources and is a major component of human skin surface lipids (oils). People ingest squalene through products such as olive oil, palm oil, rice bran and wheat germ. However, the largest concentration of squalene is found in the liver of deep sea sharks. It is now well-known that squalene is the physiological substance functioning in animal as the precursor of cholesterol biosynthesis. Furthermore, there is a long history of using squalene as an attractive resource for functional food in preventing cardiovascular disease, because it has physiological functions such as anti-hyper cholesterolemia and antioxidant[22]. Thus, our results could help explain the anti-hyper cholesterolemia and antioxidant activities of longan.

Althouth husk and kernel are often taken as by-products of Longan fruit, they account for 16-40 % of weight for the whole fruit. Present study has demonstrated that unsaturated fatty acids are the main compositions of husk and kernel. It has been reported that unsaturated fatty acids have the ability to lower thrombosis, cholesterol and blood pressure levels, reduce platelet adhesion and inhibit lipid peroxidation. For this reason, Longan husk and kernel have the potential to be used as the possible pharmaceutical supplement.

ACKNOWLEDGEMENTS

This research was supported by the Scientific and Technological Project of Shaanxi Province, China (No. 2011K12-03-01).

REFERENCES

1. T. Pholpho, S. Pathaveerat and P. Sirisomboon, *J. Food Eng*., **104**, 169 (2011).
2. Y.M. Jiang, Z.Q. Zhang, D.C. Joyce and S. Ketsa, *Postharvest Biol. Technol*., **26**, 241 (2002).
3. B. Yang, Y.M. Jiang, M.M. Zhao, F. Chen, R. Wang, Y.L. Chen and D.D. Zhang, *Food Chem.*, **115**, 609 (2009).
4. B. Yang, Y.M. Jiang, J. Shi, F. Chen and M. Ashraf, *Food Res. Int*., **44**, 1837 (2011).
5. Y.C. Chung, C.C. Lin, C.C. Chou and C.P. Hsu, *Eur. J. Clin. Invest.*, **40**, 713 (2010).
6. S.A. de Assis, J.C.R. Vellosa, I.L. Brunetti, N.M. Khalil, K.M. da Silva Cerqueira Leite, A.B.G. Martins and O.M.M. de Faria Oliveira, *J. Food Sci. Nutr. Int*., **60**, 439 (2009).
7. S.J. Park, D.H. Park, D.H. Kim, S. Lee, B.H. Yoon, W.Y. Jung, K.T. Lee, J.H. Cheong and J.H. Ryu, *J. Ethnopharmacol*., **128**, 160 (2010).
8. K.N. Prasad, J. Hao, J. Shi, T. Liu, J. Li, X.Y. Wei, S.X. Qiu, S. Xue and Y.M. Jiang, *Innov. Food Sci. Emerg. Technol*., **10**, 413 (2009).
9. N. Rangkadilok, S. Sitthimonchai, L. Worasuttayangkurn, C. Mahidol, M. Ruchirawat and J. Satayavivad, *Food Chem. Toxicol*., **45**, 328 (2007).
10. Y.Y. Soong and P.J. Barlow, *Food Chem.*, **88**, 411 (2004).
11. B. Yang, M.M. Zhao and Y.M. Jiang, *Food Chem*., **114**, 629 (2009).
12. B. Yang, M.M. Zhao, J. Shi, G.P. Cheng, N. Ruenroengklin and Y.M. Jiang, *J. Food Process Eng*., **31**, 66 (2008).
13. S. Jaitrong, N. Rattanapanone and J.A. Manthey, *Proc. Florida State Hortic. Soc*., **119**, 371 (2006).
14. N. Rangkadilok, L. Worasuttayangkurn, R.N. Bennett and J. Satayavivad, *J. Agric. Food Chem*., **53**, 1387 (2005).
15. J.Y. Shi, J. Sun, X.Y. Wei, J. Shi, G.P. Cheng, M.M. Zhao, J.S. Wang, B. Yang and Y.M. Jiang, *LWT-Food Sci. Technol*., **41**, 1742 (2008).
16. J. Sun, J. Shi, Y.M. Jiang, S.J. Xue and X.Y. Wei, *J. Agric. Food Chem*., **55**, 5864 (2007).
17. G.M. Zheng, L.X. Xu, P. Wu, H.H. Xie, Y.M. Jiang, F. Chen and X.Y. Wei, Food Chem., **116**, 433 (2009).
18. K.M. Sheng and H.J. Wang, *Chin. J. Exp. Tradit. Med. Formulae*, **16**, 236 (2010) (in Chinese).
19. G.X. Jiang, Y.M. Jiang, B. Yang, C.Y. Yu, R. Tsao, H.Y. Zhang and F. Chen, *J. Agric. Food Chem*., **57**, 9293 (2009).
20. L.G. Wen, B. Yang, C. Cui, L.J. You and M.M. Zhao, *Food Anal. Methods*, **5**, 1244 (2012).
21. C.P. Diana, J.C. Claudio, P. Gustavo and M.B. Josep, *Anal. Bioanal. Chem*., **394**, 1319 (2009).
22. H.N. Bhilwade, N. Tatewaki and H. Nishida, *Curr. Pharm. Biotechnol*., **11**, 875 (2010).