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Research Article

Chemical Constituents of *Durio zibethinus* Murr. Fruit

Consolacion Y. Ragasa[1,2*], Jariel Naomi B. Bacar[1], Maria Margarita R. Querido[1], Maria Carmen S. Tan[1], Ramon S, Del Fierro[3], Jae Sue Choi[4]

[1]*Chemistry Department, De La Salle University, 2401 Taft Avenue, Manila 1004, Philippines*
[2]*Chemistry Department, De La Salle University Science & Technology Complex Leandro V. Locsin Campus, Biñan City, Laguna 4024, Philippines*
[3]*Chemistry Department, University of San Carlos-Talamban Campus, 6000 Cebu City, Philippines*
[4]*Department of Food Science & Nutrition, Pukyong National University, 599-1 Daeyeon-3 Dong, Namgu, Busan 608-737, Republic of Korea*

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ABSTRACT
Chemical investigation of the dichloromethane extracts of *Durio zibethinus* Murr. fruit afforded monogalactosyl diacylglycerols (**1**), triacylglycerols (**2**), and a mixture of **2** and fatty acid methyl esters (**3**) from the pulp; **2**, a mixture of β-sitosterol (**4**) and stigmasterol (**5**), a mixture of phytyl fatty acid esters (**6**) and β-sitosteryl fatty acid esters (**7**), and monoacylglycerols (**8**) from the exocarp; **2**, a mixture of **4** and **5**, and β-sitosteryl-3β-glucopyranoside-6'-*O*-fatty acid esters (**9**) from the seeds and carpel. The structures of **1**-**9** were identified by comparison of their NMR data with literature data.

Keywords: *Durio zibethinus*, Bombacaceae, monogalactosyl diacylglycerols, triacylglycerols, fatty acid methyl esters, β-sitosterol, stigmasterol, phytyl fatty acid esters, β-sitosteryl fatty acid esters, monoacylglycerols. β-sitosteryl-3β-glucopyranoside-6'-*O*-fatty acid esters

INTRODUCTION

The fruit of *Durio zibethinus* Murr., commonly known as durian is a good source of carbohydrates, protein, vitamins B and C. Its pulp is eaten raw, cooked as a vegetable, frozen or dried. The seeds can be boiled or roasted and used as confections[1]. The most abundant monosaccharide in the carbohydrate composition of durian seed gum were galactose (48.6-59.9%), glucose (37.1-45.1%), arabinose (0.58-3.41%), and xylose (0.3-3.21%). The predominant fatty acid of the lipid fraction from the durian seed gum were palmitic acid (C16:0), palmitoleic acid (C16:1), stearic acid (C18:0), oleic acid (C18:1), linoleic acid (C18:2), and linolenic acid (C18:2). The most abundant amino acids of durian seed gum were: leucine (30.9-37.3%), lysine (6.04-8.36%), aspartic acid (6.10-7.19%), glycine (6.07-7.42%), alanine (5.24-6.14%), glutamic acid (5.57-7.09%), valine (4.5-5.50%), proline (3.87-4.81%), serine (4.39-5.18%), threonine (3.44-6.50%), isoleucine (3.30-4.07%), and phenylalanine (3.11-9.04%)[2]. The extracts which were analysed by capillary GC and GC-MS showed 63 constituents comprising 30 esters, 16 sulphurcontaining compounds, 5 ketones, 8 alcohols and 4 miscellaneous compounds[3]. An aroma extract dilution analysis was applied on the volatile fraction isolated from Thai durian by solvent extraction. High flavor dilution factors were exhibited by ethyl (2*S*)-2-methylbutanoate (fruity), ethyl cinnamate (honey), and 1-(ethylsulfanyl)ethanethiol (roasted onion), followed by 1-(ethyldisulfanyl)-1-(ethylsulfanyl)ethane (sulfury, onion), 2(5)-ethyl-4-hydroxy-5(2)-methylfuran-3(2*H*)-one (caramel), 3-hydroxy-4,5-dimethylfuran-2(5*H*)-one (soup seasoning), ethyl 2-methylpropanoate (fruity), ethyl butanoate (fruity), 3-methylbut-2-ene-1-thiol (skunky), ethane-1,1-dithiol (sulfury, durian), 1-(methylsulfanyl)ethanethiol (roasted onion), 1-(ethylsulfanyl)propane-1-thiol (roasted onion), and 4-hydroxy-2,5-dimethylfuran-3(2*H*)-one (caramel)[4]. We report herein the isolation of monogalactosyl diacylglycerols (**1**), triacylglycerols (**2**), and a mixture of **2** and fatty acid methyl esters (**3**) from the pulp; **2**, a mixture of β-sitosterol (**4**) and stigmasterol (**5**), a mixture of phytyl fatty acid esters (**6**) and β-sitosteryl fatty acid esters (**7**), and monoacylglycerols (**8**) from the exocarp; **2**, a mixture of **4** and **5**, and β-sitosteryl-3β-glucopyranoside-6'-*O*-fatty acid esters (**9**) from the seeds and carpel of *D. zibethinus*. The structures of **1**-**9** are presented in Fig. 1.

MATERIALS AND METHODS

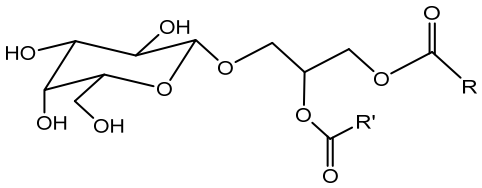
General Experimental Procedure

NMR spectra were recorded in $CDCl_3$ on a JEOL JNM ECP-400 spectrometer (Tokyo, Japan) at 400 MHz for ^1H. Column chromatography was performed with silica gel 60 (70-230 mesh). Thin layer chromatography was performed with plastic backed plates coated with silica gel F_{254} and the plates were visualized by spraying with vanillin/H_2SO_4 solution followed by warming.

General Isolation Procedure

A glass column 18 inches in height and 1.0-inch internal diameter was packed with silica gel. The crude extracts were fractionated by silica gel chromatography using

**Author for Correspondence: consolacion.ragasa@dlsu.edu.ph*



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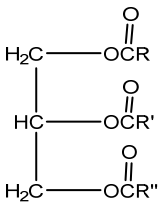

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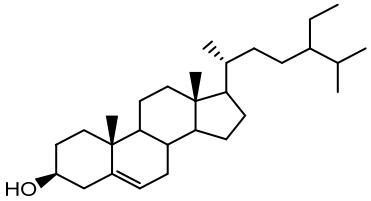
3 R, R' = long chain alkyls



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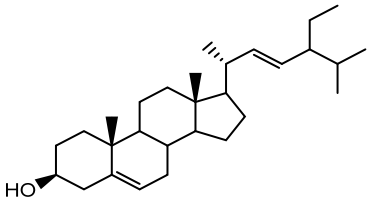

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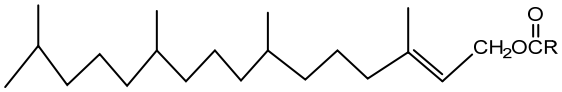

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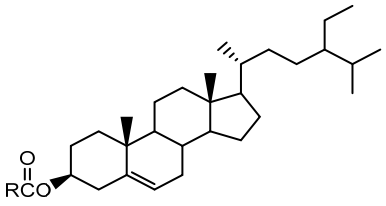

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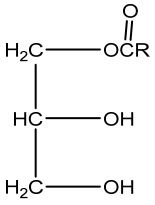

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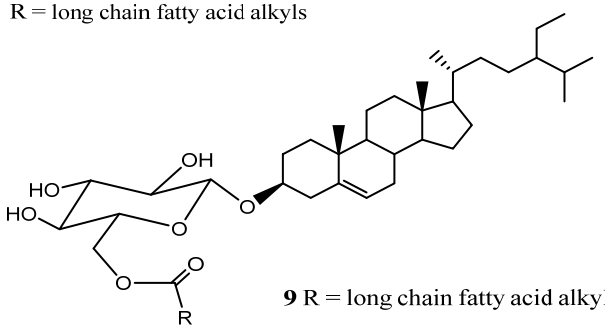

9 R = long chain fatty acid alkyls

Figure 1: Chemical structures of of monogalactosyl diacylglycerols (**1**), triacylglycerols (**2**), fatty acid methyl esters (**3**), β-sitosterol (**4**), stigmasterol (**5**), phytyl fatty acid esters (**6**), β-sitosteryl fatty acid esters (**7**), monoacylglycerols (**8**), and β-sitosteryl-3β-glucopyranoside-6'-*O*-fatty acid esters (**9**) from *D. zibethinus*.

increasing proportions of acetone in dichloromethane (10% increment) as eluents. Twenty milliliter fractions were collected. All fractions were monitored by thin layer chromatography. Fractions with spots of the same R_f values were combined and rechromatographed in appropriate solvent systems until TLC pure isolates were obtained. A glass column 12 inches in height and 0.5-inch internal diameter was used for the rechromatography. Five milliliter fractions were collected. Final purifications were conducted using Pasteur pipettes as columns. One milliliter fractions were collected. The fruit was separated into four parts namely, pulp, exocarp, seeds and carpel. Each part was chopped into small pieces, freeze-dried and then ground in a blender. The freeze-dried pulp (251.33 g), exocarp (61.98 g), seeds (86.78g), and carpel (246.53 g) were separately soaked in CH_2Cl_2 for three days and then

filtered to afford crude extracts of pulp (37.69 g), exocarp (0.55 g), seeds (1.24 g) and carpel (1.03 g).

Plant Material

The *Durio zibethinus* Murr. fruits were obtained from Davao City, Philippines in October 2015. The fruit was authenticated at the Botany Division, Philippine National Museum.

Isolation of the Chemical Constituents of the Pulp

The crude pulp extract (37.69 g) was chromatographed using increasing proportions of acetone in CH_2Cl_2 (10% increment) as eluents. The 20% acetone in CH_2Cl_2 fraction was rechromatographed (2 ×) using 5% EtOAc in petroleum ether to yield **2** (18 mg). The 30% acetone in CH_2Cl_2 fraction was rechromatographed (2 ×) using 5% EtOAc in petroleum ether to yield a mixture of **2** and **3** (8 mg). The 80% acetone in CH_2Cl_2 fractions was rechromatographed (3 ×) using CH_3CN:Et_2O:CH_2Cl_2 (2.5:2.5:5, v/v) to afford **1** (9 mg) after trituration with petroleum ether.

Isolation of the Chemical Constituents of the Exocarp

The crude exocarp extract (0.55 g) was chromatographed using increasing proportions of acetone in CH_2Cl_2 (10% increment) as eluents. The CH_2Cl_2 fraction was rechromatographed (3 ×) using 5% EtOAc in petroleum ether to afford a mixture of **6** and **7** (3 mg) after washing with petroleum ether. The 10% acetone in CH_2Cl_2 fraction was rechromatographed (2 ×) using 5% EtOAc in petroleum ether to yield **2** (12 mg) after washing with petroleum ether. The 30% acetone in CH_2Cl_2 fraction was rechromatographed (2 ×) using 10% EtOAc in petroleum ether to yield a mixture of **4** and **5** (9 mg) after washing with petroleum ether. The 50% acetone in CH_2Cl_2 fractions was rechromatographed (3 ×) using CH_3CN:Et_2O:CH_2Cl_2 (1:1:8, v/v) to afford **8** (5 mg) after trituration with petroleum ether.

Isolation of the Chemical Constituents of the Seeds

The crude seeds extract (1.24 g) was chromatographed using increasing proportions of acetone in CH_2Cl_2 (10% increment) as eluents. The 0%-20% acetone in CH_2Cl_2 fractions were combined and rechromatographed (2 ×) using 5% EtOAc in petroleum ether to afford **2** (20 mg). The 40% acetone in CH_2Cl_2 fraction was rechromatographed (3 ×) using 15% EtOAc in petroleum ether to yield a mixture of **4** and **5** (7 mg) after washing with petroleum ether. The 60% acetone in CH_2Cl_2 fraction was rechromatographed (3 ×) using CH_3CN:Et_2O:CH_2Cl_2 (2:2:6, v/v) to yield **9** (3 mg) after trituration with petroleum ether.

Isolation of the Chemical Constituents of the Carpel

The crude carpel extract (1.03 g) was chromatographed using increasing proportions of acetone in CH_2Cl_2 (10% increment) as eluents. The 10% acetone in CH_2Cl_2 fractions were combined and rechromatographed (2 ×) using 5% EtOAc in petroleum ether to afford **2** (11 mg). The 20% acetone in CH_2Cl_2 fraction was rechromatographed (3 ×) using 10% EtOAc in petroleum ether to afford **4** and **5** (7 mg) after washing with petroleum ether. The 40-50% acetone in CH_2Cl_2 fraction was rechromatographed (3 ×) using CH_3CN:Et_2O:CH_2Cl_2 (2:2:6, v/v) to yield **9** (2 mg) after trituration with petroleum ether.

RESULTS AND DISCUSSION

Silica gel chromatography of the dichloromentane extracts of *D. zibethinus* afforded **1**-**9**. The NMR spectra of **1** are in accordance with data reported in the literature for monogalactosyl diacylglycerols[5]; **2** for triacylglycerols[6], **3** for fatty acid methyl esters[7],**4** for β-sitosterol[8], **5** for stigmasterol[8], **6** for phytyl fatty acid esters[9], **7** for β-sitosteryl fatty acid esters[10], **8** for monoacylglycerols[8], and **9** for β-sitosteryl-3β-glucopyranoside-6'-*O*-fatty acid esters[11]. The ratios of the mixture of β-sitoterol (**4**) and stigmasterol (**5**) in the exocarp, seeds and carpel of *D. zibethinus* were identifed as 3.5:1, 5:1 and 4:1, respectively. The ratios were deduced from the intensities and integrations of the ^{1}H NMR resonances for olefinic protons at δ 5.35 (d, J = 4.8 Hz, H-5) and methyl protons at δ 0.66 (s, CH_3-18) for **4** and olefinic protons at δ 5.35 (d, J = 4.8 Hz, H-5), 5.13 (dd, J = 8.4, 15.6. H-22) and 5.00 (dd, J = 8.4, 15.0, H-23) and the methyl protons at δ 0.68 (s, CH_3-18) for **5**[8].

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