

# Flavonoids isolated from the fresh sweet fruit of *Averrhoa carambola*, commonly known as star fruit

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## ARTICLE INFO

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WBKKVLAYDMACSC-HPHGPOCDSA-

NChemical compounds studied in this article:

(+)-Epicatechin (PubChem CID: 182232)

Dihydrokaempferol (aromadendrin) 3-O-glucoside (PubChem CID: 10478918)

Taxifolin 3'-O-glucoside (PubChem CID: 14282774)

Galangin 3-O-rutinoside (PubChem CID: 98464939)

Isorhamnetin 3-O-rutinoside (PubChem CID: 17751019)

## ABSTRACT

Thirteen flavonoids were isolated from the fresh sweet fruit of *Averrhoa carambola* L. (Oxalidaceae), commonly known as star fruit, and their structures were determined by spectroscopic and chemical methods. 8-Carboxymethyl-(+)-epicatechin methyl ester, pinobanksin 3-O-β-D-glucoside, and carambolosides M–Q were undescribed structures. (+)-Epicatechin, aromadendrin 3-O-β-D-glucoside, helicioside A, taxifolin 3'-O-β-D-glucoside, galangin 3-O-rutinoside, and isorhamnetin 3-O-rutinoside were reported from this species for the first time. Pinobanksin 3-O-β-D-glucoside and carambolosides M–Q showed more potent 2,2'-azinobis-(3-ethylbenzthiazoline-6-sulphonic acid) (ABTS) radical cation scavenging activity (IC<sub>50</sub> = 5.3–2.3 μM) than L-ascorbic acid (10.5 μM). Further, (+)-epicatechin, pinobanksin 3-O-β-D-glucoside, isorhamnetin 3-O-rutinoside, and carambolosides O–Q exhibited weak porcine pancreatic lipase inhibitory activity.

## 1. Introduction

The fruit of *Averrhoa carambola* L. (Oxalidaceae), commonly known as star fruit or carambola, is popular in Southeast Asia countries and China with commercial value. There are mainly two types of fruit in taste, sweet or sour. Sweet star fruit can be eaten out of hand or sliced and used in salads or as garnish in cocktail drinks and beverages. Sour star fruit is often eaten with sugar (Lim, 2012). It was reported that the total flavonoid contents of four star fruit cultivars in southern China were 104–235.1 mg catechin equivalent per 100 g fresh weight (Pang et al., 2016). However, with respect to their structures from star fruit, only cyanidin 3-O-β-D-glucoside, cyanidin 3,5-di-O-β-D-glucoside (Gunasegaran, 1992), procyanidin B<sub>2</sub>, (–)-epicatechin, and isoquercitrin (Pang et al., 2016; Gunawardena et al., 2015) were reported. Our previous studies on dried star fruit in sour taste yielded ten phloretin C-glycosides, carambosides A–J, and three known flavonoid glycosides, carambolaflavone, hovertichoside C, and isovitexin 2''-O-α-

L-rhamnoside (Yang et al., 2015, 2016). The objective of this study was to clarify the structures of flavonoids present in fresh sweet star fruit. As a result, thirteen flavonoids were obtained, including undescribed a flavan-3-ol (1), a dihydroflavon-3-ol glucoside (3), five phloretin C-glycosides (9–13), and six known compounds, which were not previously reported from this species. This paper describes the isolation, structural elucidation, and evaluation of antioxidant and pancreatic lipase inhibitory activities of these flavonoids.

## 2. Results and discussion

The 95% aqueous ethanol extract of fresh star fruit in sweet taste was separated by solvent fractionation, column chromatography (CC), and liquid chromatography (LC) to afford compounds 1–13 (Fig. 1).

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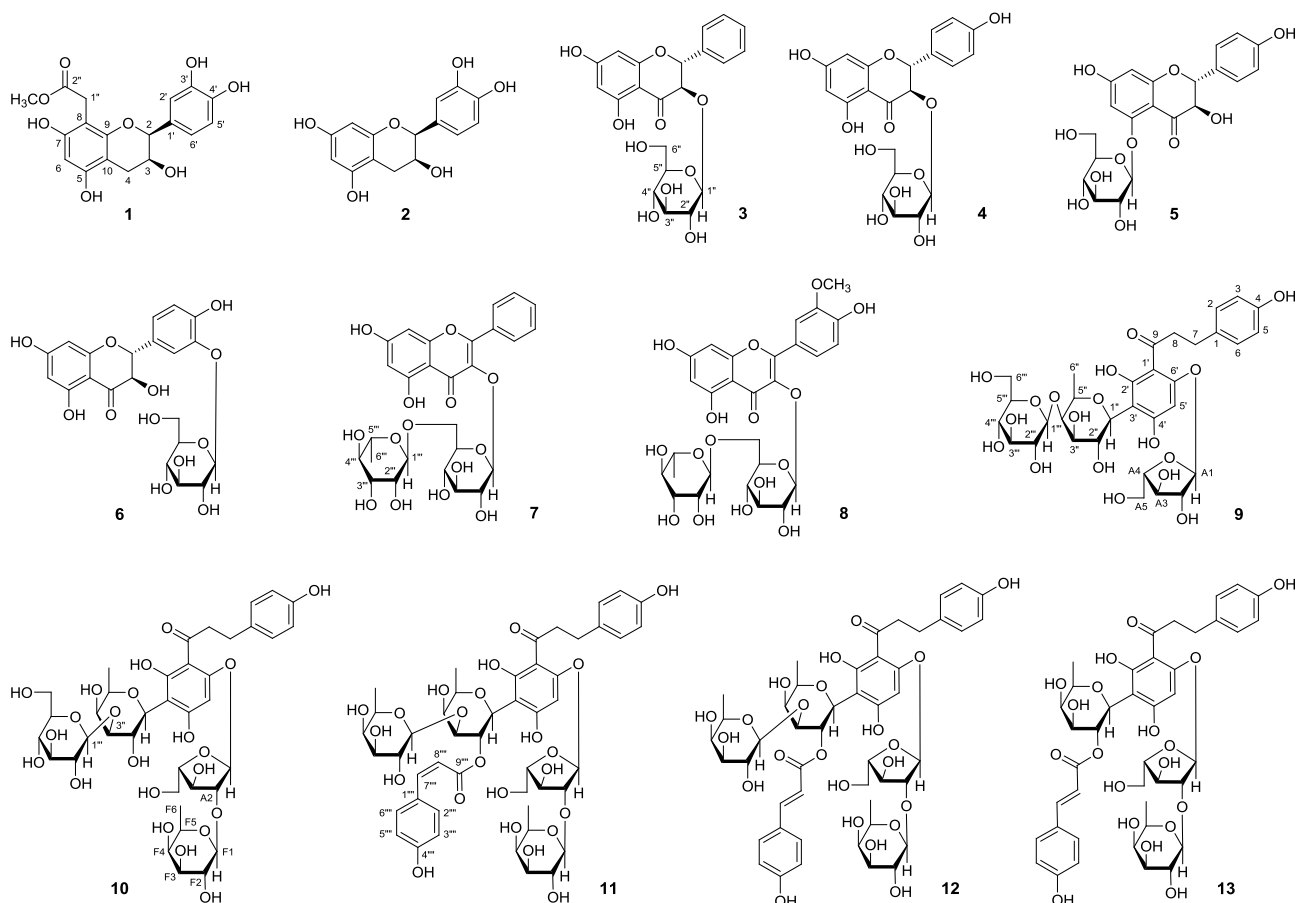


Fig. 1. Structures of compounds 1–13.

## 2.1. Structural elucidation

Compound **1** was deduced to have the molecular formula  $C_{18}H_{18}O_8$  from its high resolution electrospray ionization mass spectrometry (HRESIMS) and NMR data. The  $^1H$  and  $^{13}C$  NMR spectra exhibited signals of a singlet proton (H-6), three ABX-coupled aromatic protons (H-2', H-5', and H-6'), twelve aromatic carbons (C-5–10 and C-1'–6'), in addition to four protons and three carbons assignable for a  $-OCH_2OCH_2-$  part. These signals were typical of an epicatechin moiety with C-6 or C-8 being substituted (Xu et al., 2010). In the heteronuclear multiple bond correlation (HMBC) spectrum, the correlations from two protons of an isolated methylene (H<sub>2</sub>-1'') to C-7, C-8, C-9, and a carboxyl carbon (C-2''), and from three singlet protons of a methoxyl group to C-2'' ascertained the presence of an acetic acid methyl ester moiety and its connection to C-8 via carbon bond (Tian et al., 2014). However, the optical rotation ( $\alpha_D$ ) value of **1** was positive, and its electronic circular dichroism (ECD) spectrum showed positive Cotton effects at 208 (+4.3), 219 (+2.2), and 278 (+0.3) nm ( $\Delta\epsilon$ ), which were opposite to those of (–)-epicatechin (Yanagida et al., 2016). Further, the ECD calculation result (Fig. 2) also revealed the 2S, 3S absolute configurations. Thus, compound **1** was identified as 8-carboxymethyl-(+)-epicatechin methyl ester.

Compound **3** was determined the molecular formula  $C_{21}H_{22}O_{10}$  based on its NMR and HRESIMS data. The  $^1H$  and  $^{13}C$  NMR spectra demonstrated signals of five aromatic protons assignable for a mono-substituted phenyl (H-2'–H-6') and two *ortho*-coupled aromatic protons (H-6 and H-8) for the other phenyl, in addition to signals of two oxygenated methines (OCH-2 and OCH-3), a carbonyl carbon (C-4), and a  $\beta$ -glucosyl moiety. The HMBC correlations from H-2 to C-3, C-4, C-9, C-1', and C-2'/6', H-3 to C-2, C-4, C-10, and C-1', as well as from H-1'' to

C-3 and H-3' to C-1'' clarified the presence of 3,5,7-trihydroxydihydroflavone aglycone (Biva et al., 2016) and the connection of glucosyl moiety to C-3. The coupling constant of 9.8 Hz between H-2 and H-3 clarified their *trans* relative configurations. Consistence of its CD spectrum with that of (2R, 3R)-dihydrokaempferol 3-O- $\beta$ -D-glucoside (Gödecke et al., 2005) and its ECD calculation result (Fig. 2) revealed the 2R, 3R absolute configurations. Acid hydrolysis of **3** released D-glucose [retention time ( $t_R$ ) = 21.2 min], which was identified by comparison of its HPLC  $t_R$  value with those of authentic D-(+)-glucose ( $t_R$  = 21.3 min) and L-(–)-glucose ( $t_R$  = 19.3 min) (Fig. S33). Hence, compound **3** was established as pinobanksin 3-O- $\beta$ -D-glucoside.

The molecular formula  $C_{32}H_{42}O_{18}$  of compound **9** was decided from its HRESIMS and NMR data. The  $^1H$  and  $^{13}C$  NMR and hetero-nuclear singular quantum correlation (HSQC) spectra (Table 1) showed signals of two aliphatic methylenes (CH<sub>2</sub>-7 and CH<sub>2</sub>-8), twelve aromatic carbons (C-1–6 and C-1'–6'), and a carbonyl carbon (C-9), which were characteristic of a dihydrochalcone skeleton. Excluding the signals assigned for the skeleton, comparison of the  $\delta$  values of remaining seventeen carbons and the  $\delta$  and  $J$  values of remaining protons with those of carambolasides C and Ia, which were previously obtained from dried star fruit in sour taste (Yang et al., 2015, 2016), declared the presence of a  $\beta$ -fucosyl, a  $\beta$ -glucosyl, and an  $\alpha$ -arabifuranosyl moiety. In the HMBC spectrum, the correlations from H-1'' to C-2', C-3', and C-4', H-1''' to C-4'', H-4''' to C-1'', and H-A1 to C-6' clarified the direct connection of C-1'' to C-3' and the connections of C-1''' to C-4'' and C-A1 to C-6' via oxygen bridges. Acid hydrolysis of **9** yielded D-glucose ( $t_R$  = 21.2 min) and L-arabinose ( $t_R$  = 23.7 min), which were determined by comparison of their HPLC  $t_R$  values with authentic sugars (Fig. S34). The  $\beta$ -fucosyl moiety connected to phloretin aglycone through carbon bond from this species was previously determined to possess D absolute configuration

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