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New Sesquiterpenoids from *Eugenia jambolana* Seeds and Their Anti-microbial Activities

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Supporting Information

ABSTRACT: Twenty four sesquiterpenoids, **1**−**24**, including 11 new sesquiterpenoids, jambolanins A−K, and two new norsesquiterpenoids, jambolanes A and B, along with six known triterpenoids, were isolated from the seeds of *Eugenia jambolana* fruit. Their structures were elucidated on the basis of NMR and MS spectrometry data analysis. Among the isolates, compound **13** possessed a rare 6,7-*seco*-guaiene skeleton, and compounds **14** and **15** were norsesquiterpenoids containing a spiro[4.4]nonane skeleton. Antimicrobial assay evaluation revealed that sesquiterpenoids, **4**, **5**/**6**, **17**, **19**, **21**, **23**, and **24** inhibited the growth of the Gram-positive bacterium, *Staphylococcus aureus*. The current study advances scientific knowledge of *E. jambolana* phytochemicals and suggests that its sesquiterpenoids may contribute, in part, to the anti-infective effects attributed to the edible fruit of this plant.

KEYWORDS: *Eugenia jambolana, Myrtaceace, sesquiterpenoids, antimicrobial activity*

INTRODUCTION

Eugenia jambolana Lam. (syn. *Syzygium cumini* Skeels; *Syzygium jambolanum*), a member of the Myrtaceace family, occurs mainly in tropical and subtropical regions of the world. The ripe fruit of *E. jambolana* is an edible purple berry commonly known as jamun, black plum, or Indian blackberry.[1] In the past few decades, *E. jambolana* has gained considerable scientific attention due to its health-beneficial effects particularly in preventing/treating diabetes and multiple infection related diseases, such as diarrhea, bronchitis, fever, and pharyngitis.[2,3] The fruit pulp and seeds of *E. jambolana* have been used in various food preparations, herbal medicines, and botanical dietary supplements because of their nutraceutical and therapeutic values.[1,4] Previous phytochemical and biological studies on *E. jambolana* have mainly focused on its phenolics constituents and their evaluation for potential antidiabetic effects.[3] In the course of our investigation of *E. jambolana*, we have reported on anthocyanins present in its fruit pulp and their antiproliferative effects against breast cancer cells.[5,6] In addition, we have identified several hydrolyzable tannins and flavonoids with α-glucosidase inhibitory effects,[1] as well as 16 phloroglucinols with protein tyrosine phosphatase 1B inhibitory activities from *E. jambolana* seeds.[7]

However, to date, there is limited knowledge on the "nonphenolic" constituents, including terpenoids, present in this plant. Terpenes are a class of naturally occurring substances implicated with multiple biological effects of many foods and medicinal plants.[8,9] Moreover, the Myrtaceae family is known for several of its species which produces important volatile oils and terpenes.[10−12] The essential oils of *E. jambolana*, which are enriched with mono- and sesquiterpenoids, have been reported to have antimicrobial,[13] anti-inflammatory,[14] antileishmania,[15] and antioxidant activity.[13] The terpenoid constituents of different parts of *E. jambolana* have mainly been investigated by gas chromatography−mass spectrometry (GC-MS), leading to the identification of monoterpenes including α-, β-, and γ-pinene, myrtenal, *cis*- and *trans*-ocimene,[16−18] and sesquiterpenes such as caryophyllene.[13] Our group recently reported, for the first time, the isolation by column chromatography and structure elucidation by NMR of 14 triterpenoids from the fruit pulp extract of *E. jambolana*.[19]

In continuation of our efforts to increase scientific knowledge of the phytochemical constituents of *E. jambolana* and to better understand its usage in regard to antibacterial effects, we conducted the current study. Herein, we report the isolation and identification of 24 sesquiterpenoids, **1**−**24**, including 11 new sesquiterpenoids and two new norsesquiterpenoids, along with six known triterpenoids from *E. jambolana* seeds. In addition, the isolated sesquiterpenoids were evaluated for their antimicrobial effects.

MATERIALS AND METHODS

General Experimental Procedures. The optical rotations were recorded in CH_3OH on a MCP200 automatic polarimeter (Anton Paar, Graz, Austria). Ultraviolet spectra were measured with a DU 730 nucleic acid/protein analyzer (Beckman Coulter Inc., Brea, CA). IR spectra were recorded with a Tensor 27 FT-IR spectrometer (film) (Bruker Optik GmbH, Ettlingen, Germany). 1D and 2D NMR spectra

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Table 1. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) Data for Compounds 1−4[a]

	1		2		3		4	
position	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)
1	80.5, C		80.2, C		46.1, CH	2.64 (m)	43.1, CH	3.35 (m)
2	50.0, CH_2	2.33 (d, 17.9, Hα)	49.9, CH_2	2.22 (d, 18.0, Hα)	42.0, CH_2	2.05 (dd, 18.4, 2.0, Hα)	39.6, CH_2	2.42 (dd, 18.5, 6.9, Hα)
		2.52 (d, 17.9, Hβ)		2.60 (d, 18.0, Hβ)		2.02 (dd, 18.4, 2.0, Hβ)		2.17 (dd, 18.5, 4.6, Hβ)
3	204.0, C		205.4, C		207.6, C		208.0, C	
4	140.5, C		135.4, C		134.8, C		135.6, C	
5	164.1, C		167.0, C		168.6, C		167.3, C	
6	59.1, CH	3.80 (s)	116.5, CH	6.12 (s)	117.4, CH	6.67 (s)	117.5, CH	6.72 (s)
7	70.7, C		159.7, C		163.8, C		163.0, C	
8	21.1, CH_2	1.87 (m)	28.4, CH_2	2.45 (m, Hα)	25.2, CH_2	2.26 (dd, 17.0, 10.8, Hα)	26.4, CH_2	2.55 (m, Hα)
				2.20 (m, Hβ)		2.44 (dd, 17.0, 7.8, Hβ)		2.29 (m, Hβ)
9	24.0, CH_2	2.01 (m, Hα)	30.4, CH_2	2.26 (m, Hα)	35.5, CH_2	1.56 (m, Hα)	35.0, CH_2	2.08 (m, Hα)
		1.29 (m, Hβ)		1.27 (m, Hβ)		1.69 (m, Hβ)		1.32 (m, Hβ)
10	38.9, CH	2.01 (m)	39.4, CH	2.14 (m)	38.7, CH	1.53 (m)	32.5, CH	2.11 (m)
11	36.2, CH	1.66 (m)	38.8, CH	2.43 (m)	71.3, C		73.3, C	
12	18.3, CH_3	0.99 (d, 6.8)	21.7, CH_3	1.04 (d, 6.8)	28.8, CH_3	1.27 (s)	28.8, CH_3	1.26 (s)
13	18.4, CH_3	0.93 (d, 6.8)	21.7, CH_3	1.05 (d, 6.8)	29.0, CH_3	1.27 (s)	28.9, CH_3	1.26 (s)
14	13.7, CH_3	0.57 (d, 7.1)	15.4, CH_3	0.71 (d, 7.0)	22.2, CH_3	1.01 (d, 6.6)	15.0, CH_3	0.62 (d, 6.9)
15	7.6, CH_3	1.75 (s)	8.2, CH_3	1.63 (s)	8.5, CH_3	1.64 (s)	8.4, CH_3	1.65 (s)
OH-1		4.64 (s)		5.13 (s)				
OH-11						4.84 (s)		4.85 (s)

[a]Compounds **1**, **3** and **4** were measured in DMSO-d_6, and compound **2** in $CDCl_3$.

were collected on an Advance III-600 MHz spectrometer (Bruker Co., Rheinstetten, Germany) with deuterated chloroform ($CDCl_3$) or dimethyl sulfoxide (DMSO-d_6) as solvents. HRESIMS were performed using a Micro TOF-Q mass spectrometer (Bruker Daltonics, Billerica, MA). Silica gel (100−200 mesh, 300−400 mesh) (Qingdao Marine Chemical Ltd., Qingdao, China), Sephadex LH-20 (GE Healthcare Biosciences AB, Uppsala, Sweden), MCI gel (CHP-20P) (Mitsubishi Chemical Corporation, Tokyo, Japan), ODS-A (S-50 μm, 12 nm) (YMC Co., Ltd., Kyoto, Japan) were used for column chromatography. Semipreparative HPLC was performed using an ODS column (250 mm × 10 mm i.d., 5 μm, YMC-ODS-A) (YMC, Co. Ltd., Kyoto, Japan). Unless otherwise specified, all chemicals and solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shenyang, People's Republic of China).

Extraction and Isolation. Freeze-dried *E. jambolana* seed powder was provided by Verdure Science (Noblesville, IN) with an accompanying deposited voucher specimen (Accession # EJLH1) as previously reported.[7] The seed powder (5.5 kg) was initially defatted with petroleum ether (PE, 10 L × 2), and the residue was then exhaustively extracted by soaking in 70% aqueous acetone (10 L) for four times at room temperature. The solvent was evaporated *in vacuo*, and the resulting 70% acetone extract (1.2 kg) was partitioned between ethyl acetate (EtOAc, 2.5 L × 5) and H_2O (2.5 L). After solvent removal, the EtOAc extract (185.0 g) was purified on a MCI gel CHP-20P column (60 cm × 12.0 cm i.d.), eluting with H_2O/MeOH (1:0 to 0:1, v/v, 4 L solvent were used for each gradient elution system), and finally with acetone, to yield seven fractions. The 80% MeOH fraction (15.0 g) was chromatographed over a silica gel column (50 cm × 6.0 cm i.d., PE/acetone, 12:1 to 0:1, 1.2 L solvent were used for each gradient elution system) to yield 9 fractions (Fr. A-I), which were combined on the basis of thin layer chromatography analysis. Fr. B (630 mg) was applied to a silica gel column (50 cm × 2.5 cm i.d., CH_2Cl_2/EtOAc, 40:1 to 1:1, 550 mL solvent were used for each gradient elution system) to afford eight subfractions (B1−8). Subfraction B2 (11.2 mg) was separated on silica gel column (30 cm × 1.0 cm i.d.), eluted with PE/EtOAc (10:1, 300 mL solvent were used for the elution system), and further purified by semipreparative HPLC (250 mm × 10 mm i.d.) with a gradient elution system of MeOH/H_2O (62:38 to 75:25, at a flow rate of 10.0 mL/min) to afford compounds **14** (1.5 mg) and **20** (1.6 mg). Similarly, subfraction B4 (41.1 mg) was chromatographed on a silica gel column (30 cm × 1.6 cm i.d., PE/EtOAc, 8:1 to 5:1, 500 mL solvent were used for each gradient elution system) and semipreparative HPLC (250 mm × 10 mm i.d., MeOH/H_2O, 65:35, at a flow rate of 10.0 mL/min) to yield compounds **12** (1.7 mg) and **15** (3.7 mg). Subfraction B7 (35.2 mg) was fractionated by a silica gel column (30 cm × 1.6 cm i.d.) with PE/EtOAc (12:1 to 8:1, 600 mL solvent were used for each gradient elution system) and further purified by MPLC (45 cm × 4.0 cm i.d., MeOH/H_2O 70:30, flow rate = 10.0 mL/min, 800 mL solvent were used for the elution system) to yield compounds **1** (8.2 mg) and **8** (1.7 mg). Fr. C (1.27 g) was purified on a silica gel column (50 cm × 3.0 cm i.d.) with a gradient solvent system of CH_2Cl_2/EtOAc (20:1 to 1:1, 700 mL solvent were used for each gradient elution system), then further purified by semipreparative HPLC (250 mm × 10 mm i.d.), eluted with MeOH/H_2O (62:38, flow rate = 10.0 mL/min), to yield compounds **2** (2.8 mg), **4** (5.3 mg), a mixture of **5** and **6** (8.0 mg), and **16** (41.1 mg). Fr. D (1.50 g) was loaded on a Sephadex LH-20 column (130 cm × 3.0 cm i.d.) with MeOH (500 mL) as eluent to give three subfractions (D1−3). Subfraction D1 (280 mg) was separated on a silica gel column (40 cm × 2.0 cm i.d., CH_2Cl_2/acetone, 40:1 to 5:1, 500 mL solvent were used for each gradient elution system) and further purified by semipreparative HPLC (250 mm × 10 mm i.d., MeOH/H_2O, 55:45, v/v, at a flow rate of 10.0 mL/min) to yield compounds **3** (1.6 mg), **9** (2.8 mg), **10** (9.4 mg), **11** (3.5 mg), **13** (2.0 mg), **17** (3.4 mg) and **21** (2.0 mg). Similarly, subfraction D2 (680 mg) was purified on a silica gel column chromatography (50 cm × 2.5 cm i.d.) with a gradient solvent system of CH_2Cl_2/acetone (40:1 to 5:1, 800 mL solvent were used for each gradient elution system), then by MPLC (45 cm × 4.0 cm i.d., MeOH/H_2O, 70:30, flow rate = 10.0 mL/min, 1.0 L solvent were used for the elution system) to yield compounds **7** (2.5 mg), **18** (12.0 mg), **19** (4.0 mg), **22** (2.3 mg), **23** (77.0 mg) and **24** (11.8 mg).

Jambolanin A, 1. colorless oil; $[\alpha]_D^{20}$ 24 (*c* 1.0, MeOH); UV_{max} (MeOH) λ_{max} (log ε) 244 (4.14) nm; IR (film) ν_{max} 3514, 2963, 2919, 2880, 2852, 1709, 1645, 1458, 1385, 1331, 1232, 1192, 1151, 1013, 962, 890, 853 cm^{-1}; ^{1}H NMR and ^{13}C NMR data (Table 1); HRESIMS *m*/*z* 251.1656 $[M + H]^+$ (calcd. for $C_{15}H_{23}O_3$, 251.1647).

Jambolanin B, 2. light yellow oil; $[\alpha]_D^{20}$ 200 (*c* 0.56, MeOH); UV_{max} (MeOH) λ_{max} (log ε) 292 (4.87) nm; IR (film) ν_{max} 3421, 2961, 2919, 2874, 2854, 1688, 1630, 1464, 1383, 1331, 1278, 1231, 1010, 954, 872 cm^{-1}; ^{1}H NMR and ^{13}C NMR data (Table 1); HRESIMS *m*/*z* 235.1738 $[M + H]^+$ (calcd. for $C_{15}H_{23}O_2$, 235.1698).

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Table 2. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) Data for Compounds 5−8 in DMSO-d_6

	5		6		7		8	
position	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)
1	141.4, C		141.1, C		43.6, CH	2.19 (td, 11.0, 7.8)	44.7, CH	2.82 (m)
2	203.7, C		204.2, C		26.7, CH_2	1.52 (m, Hα)	23.7, CH_2	1.48 (m, Hα)
						1.72 (m, Hβ)		1.65 (m, Hβ)
3	51.5, CH_2	2.41 (d, 17.5)	50.8, CH_2	2.39 (d, 17.4)	41.1, CH_2	1.66 (m, Hα)	36.7, CH_2	1.48 (m, Hα)
		2.36 (d, 17.5)		2.34 (d, 17.4)		1.48 (m, Hβ)		1.76 (m, Hβ)
4	74.5, C		74.8, C		79.9, C		85.0, C	
5	165.7, C		165.9, C		61.1, CH	1.67 (m)	80.7, C	
6	115.4, CH	6.14 (s)	115.4, CH	6.12 (s)	70.4, CH	4.11 (dd, 7.4, 3.6)	73.3, CH	4.01 (s)
7	163.7, C		163.8, C		51.0, CH	1.42 (ddd, 10.0, 3.6, 1.6)	148.5, C	
8	27.7, CH_2	2.36 (m)	27.4, CH_2	2.34 (m)	21.7, CH_2	1.66 (m, Hα)	122.9, CH	5.49 (dd, 9.6, 5.0)
						1.56 (m, Hβ)		
9	29.6, CH_2	1.49 (m)	29.3, CH_2	1.51 (m)	38.3, CH_2	2.00 (m, Hα)	33.1, CH_2	2.62 (m, Hα)
		1.75 (m)		1.76 (m)		2.52 (m, Hβ)		1.94 (m, Hβ)
10	28.7, CH	2.80 (m)	29.0, CH	2.80 (m)	153.7, C		33.4, CH	1.91 (m)
11	38.8, CH	2.48 (m)	38.8, CH	2.48 (m)	73.0, C		36.7, CH	2.24 (m)
12	21.5, CH_3	1.07 (d, 6.9)	21.4, CH_3	1.07 (d, 6.9)	28.5, CH_3	1.20 (s)	22.5, CH_3	1.00 (d, 6.7)
13	22.0, CH_3	1.07 (d, 6.9)	21.8, CH_3	1.07 (d, 6.9)	29.2, CH_3	1.15 (s)	21.7, CH_3	0.98 (d, 6.7)
14	19.6, CH_3	0.95 (d, 6.7)	19.9, CH_3	0.94 (d, 6.4)	107.1, CH_2	4.65 (s)	14.7, CH_3	0.96 (d, 7.2)
						4.68 (s)		
15	28.5, CH_3	1.30 (s)	28.2, CH_3	1.30 (s)	24.6, CH_3	1.20 (s)	22.1, CH_3	1.16 (s)
OH-4		5.20 (s)		5.18 (s)		4.42 (s)		5.31 (s)
OH-5								2.85 (s)
OH-6						4.17 (s)		4.81 (s)
OH-11						4.21 (s)		

Table 3. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) Data for Compounds 9−11 and 13 in DMSO-d_6

	9		10		11		13	
position	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)
1	52.9, CH	3.26 (m)	52.3, CH	2.82 (dt, 8.9, 5.6)	56.2, CH	2.25 (m)	47.0, CH	2.92 (m)
2	21.8, CH_2	1.45 (m)	22.2, CH_2	1.43 (m)	22.6, CH_2	1.64 (m)	35.1, CH_2	1.53 (ddd, 13.5, 9.3, 7.2)
		1.79 (m)		1.87 (m)		1.78 (m)		2.04 (m)
3	41.6, CH_2	2.29 (t, 7.7)	41.5, CH_2	2.32 (m)	40.7, CH_2	2.26 (m)	78.9, CH	4.59 (m)
						2.32 (m)		
4	208.7, C		208.8, C		207.5, C		164.7, C	
5	204.1, C		203.3, C		204.1, C		138.7, C	
6	127.3, CH	5.69 (s)	126.4, CH	6.08 (s)	124.3, CH	6.05 (s)	190.4, CH	9.98 (s)
7	166.1, C		170.9, C		166.9, C		214.4, C	
8	68.2, CH	4.30 (m)	27.5, CH_2	2.34 (m)	24.6, CH_2	2.39 (m)	38.3, CH_2	2.31 (ddd, 17.3, 8.8, 6.6)
				2.53 (m)				2.44 (ddd, 17.3, 9.1, 5.4)
9	41.3, CH_2	1.26 (m, Hα)	36.8, CH_2	0.86 (m)	34.1, CH_2	1.52 (m)	25.3, CH_2	0.98 (m)
		2.15 (m, Hβ)		2.17 (m)		1.61 (m)		1.22 (m)
10	28.5, CH	2.21 (m)	32.9, CH	2.04 (m)	33.3, CH	1.57 (m)	34.3, CH	1.67 (m)
11	35.1, CH	2.50 (m)	72.6, C		71.3, C		40.2, CH	2.55 (m)
12	22.0, CH_3	1.02 (d, 6.8)	28.4, CH_3	1.24 (s)	27.7, CH_3	1.24 (s)	18.5, CH_3	0.96 (d, 6.9)
13	21.6, CH_3	1.04 (d, 6.8)	28.8, CH_3	1.24 (s)	28.0, CH_3	1.24 (s)	18.6, CH_3	0.96 (d, 6.9)
14	16.9, CH_3	0.74 (d, 6.8)	16.5, CH_3	0.67 (d, 6.7)	19.1, CH_3	1.04 (d, 6.5)	18.7, CH_3	0.80 (d, 6.9)
15	30.2, CH_3	2.05 (s)	30.1, CH_3	2.06 (s)	29.0, CH_3	2.04 (s)	11.7, CH_3	2.10 (s)
OH-3								5.25 (d, 6.8)
OH-8		5.26 (d, 5.0)						
OH-11				4.86 (s)		4.85 (s)		

Jambolanin C, 3. colorless oil; $[\alpha]_D^{20}$ −70 (c 0.4, MeOH); UV_{max} (MeOH) λ_{max} (log ε) 292 (4.20) nm; IR (film) ν_{max} 3408, 2958, 2924, 2860, 1723, 1676, 1625, 1586, 1461, 1384, 1355, 1290, 1231, 1173, 1128, 1068, 958 cm^{-1}; ^{1}H NMR and ^{13}C NMR data (Table 1); HRESIMS m/z 235.1725 $[M + H]^+$ (calcd. for $C_{15}H_{23}O_2$, 235.1698).

Jambolanins D/E, 5/6. colorless oil; UV_{max} (MeOH) λ_{max} (log ε) 300 (4.52) nm; IR (film) ν_{max} 3418, 2963, 2926, 2873, 1676, 1602, 1458, 1383, 1279, 1233, 1139, 1065, 956, 887 cm^{-1}; ^{1}H NMR and ^{13}C NMR data (Table 2); HRESIMS m/z 235.1749$[M + H]^+$ (calcd. for $C_{15}H_{23}O_2$, 235.1698).

Jambolanin F, 7. colorless oil; $[\alpha]_D^{20}$ 8 (c 0.5, MeOH); UV_{max} (MeOH) λ_{max} (log ε) 293 (3.86) nm; IR (film) ν_{max} 3375, 2958, 2929, 2873, 1462, 1376, 1288, 1140, 1076, 971, 886, 802 cm^{-1}; ^{1}H NMR and ^{13}C NMR data (Table 2); HRESIMS m/z 531.3710 $[2M+Na]^+$ (calcd. for $C_{30}H_{52}O_6Na$, 531.3662).

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Table 4. ^{1}H NMR (600 MHz) and ^{13}C NMR (150 MHz) Data for Compounds 14 and 15 in DMSO-d_6

	14		15	
position	δ_C, type	δ_H (J in Hz)	δ_C, type	δ_H (J in Hz)
1	221.5, C		220.7, C	
2	39.0, CH_2	2.40 (ddd, 18.2, 8.2, 2.3, Hα)	37.8, CH_2	2.31 (m, Hα)
		2.24 (ddd, 18.2, 10.5, 8.6, Hβ)		2.23 (m, Hβ)
3	29.1, CH_2	1.67 (m, Hα)	28.6, CH_2	1.98 (m, Hα)
		1.89 (m, Hβ)		1.40 (td, 12.4, 8.2, Hβ)
4	43.6, CH	2.19 (m)	38.8, CH	2.39 (m)
5	64.4, C		65.4, C	
6	36.7, CH_2	1.71 (m)	27.3, CH_2	1.47 (dt, 13.1, 9.3)
		2.11 (dt, 12.7, 9.4)		2.00 (m)
7	38.9, CH_2	2.48 (m)	39.4, CH_2	2.49 (m)
		2.66 (m)		2.56 (m)
8	168.8, C		167.4, C	
9	140.4, C		139.0, C	
10	16.7, CH_3	0.83 (d, 7.0)	14.1, CH_3	0.91 (d, 6.9)
11	188.5, CH	9.81 (s)	187.8, CH	9.80 (s)
12	15.2, CH_3	2.20 (s)	14.8, CH_3	2.20 (s)

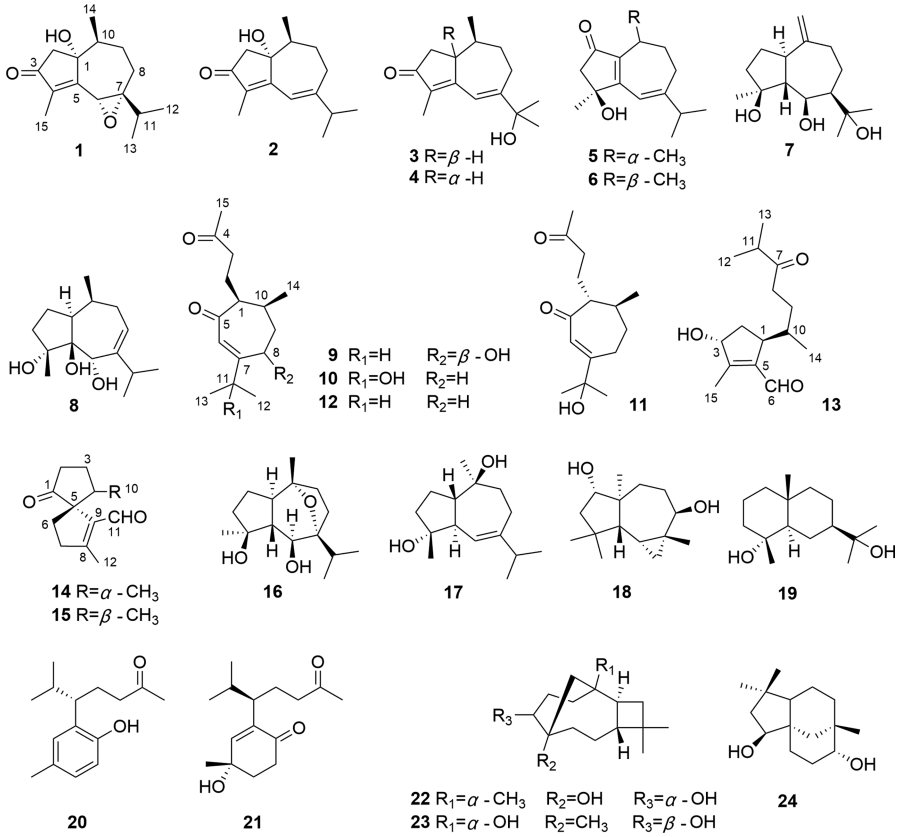

Figure 1. Structures of compounds 1−24.

Jambolanin G, 8. white amorphous power; $[\alpha]_D^{20}$ 47 (c 0.34, MeOH); UV$_{max}$ (MeOH) λ_{max} (log ε) 211 (3.54) nm; IR (film) ν_{max} 3355, 2957, 2928, 2871, 1460, 1373, 1346, 1300, 1120, 1090, 1027, 1001, 931, 864, 789, 696 cm^{-1}; ^{1}H NMR and ^{13}C NMR data (Table 2); HRESIMS m/z 509.3839 [2M+H]$^+$ (calcd. for $C_{30}H_{53}O_6$ 509.3842).

Jambolanin H, 9. colorless oil; $[\alpha]_D^{20}$ 21 (c 0.56, MeOH); UV$_{max}$ (MeOH) λ_{max} (log ε) 233 (4.68) nm; IR (film) ν_{max} 3437, 2961, 2926, 2874, 1713, 1659, 1461, 1374, 1276, 1164, 1123, 1075, 1031, 974, 801 cm^{-1}; ^{1}H NMR and ^{13}C NMR data (Table 3); HRESIMS m/z 253.1851 [M + H]$^+$ (calcd. for $C_{15}H_{25}O_3$, 253.1804).

Jambolanin I, 10. colorless oil; $[\alpha]_D^{20}$ −28 (c 1.0, MeOH); UV$_{max}$ (MeOH) λ_{max} (log ε) 233 (4.67) nm; IR (film) ν_{max} 3451, 2969, 2921, 2875, 1711, 1654, 1443, 1360, 1161, 957, 876 cm^{-1}; ^{1}H NMR and ^{13}C NMR data (Table 3); HRESIMS m/z 275.1624 [M + Na]$^+$ (calcd. for $C_{15}H_{24}O_3Na$, 275.1623).

Jambolanin J, 11. colorless oil; $[\alpha]_D^{20}$ −20 (c 0.6, MeOH); UV$_{max}$ (MeOH) λ_{max} (log ε) 233 (4.63) nm; IR (film) ν_{max} 3454, 2964, 2928, 1712, 1660, 1463, 1363, 1284, 1166, 1077, 953, 876 cm^{-1}; ^{1}H NMR and ^{13}C NMR data (Table 3); HRESIMS m/z 275.1632 [M + Na]$^+$ (calcd. for $C_{15}H_{24}O_3Na$, 275.1623).

Jambolanin K, 13. colorless oil; $[\alpha]_D^{20}$ −30 (c 0.4, MeOH); UV$_{max}$ (MeOH) λ_{max} (log ε) 245 (4.23) nm; IR (film) ν_{max} 3433, 2962, 2929,

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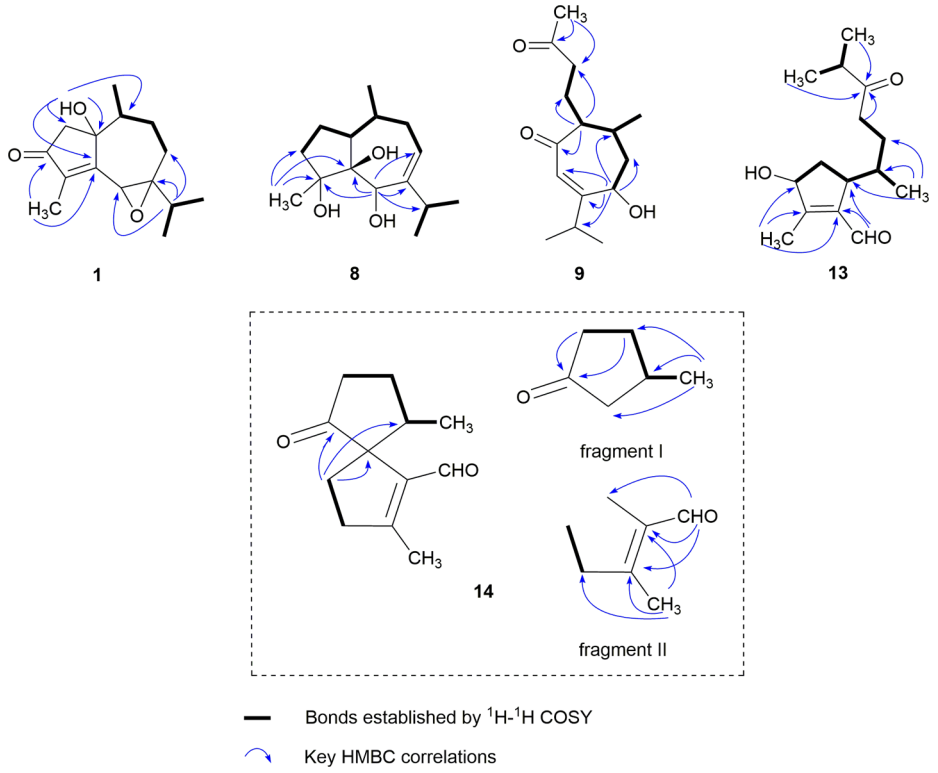

Figure 2. Key $^{1}H-^{1}H$ COSY and HMBC correlations of compounds **1**, **8**, **9**, **13**, and **14**.

2874, 1708, 1667, 1464, 1378, 1267, 1182, 1125, 1075, 1042 cm^{-1}; ^{1}H NMR and ^{13}C NMR data (Table 3); HRESIMS *m/z* 253.1840 $[M + H]^+$ (calcd. for $C_{15}H_{25}O_3$, 253.1804).

Jambolane A, 14. colorless oil; $[\alpha]_D^{20}$ 24 (*c* 0.5, MeOH); UV_{max} (MeOH) λ_{max} (log ε) 234 (3.69), 246 (3.75) nm; IR (film) ν_{max} 2955, 2925, 2855, 1731, 1669, 1569, 1455, 1405, 1380, 1295, 1262, 1121, 1039, 801 cm^{-1}; ^{1}H NMR and ^{13}C NMR data (Table 4); HRESIMS *m/z* 193.1225 $[M + H]^+$ (calcd. for $C_{12}H_{17}O_2$, 193.1229).

Jambolane B, 15. colorless oil; $[\alpha]_D^{20}$ 22 (*c* 0.74, MeOH); UV_{max} (MeOH) λ_{max} (log ε) 234 (3.72), 258 (3.81) nm; IR (film) ν_{max} 2957, 2918, 2873, 1736, 1660, 1631, 1466, 1440, 1378, 1347, 1274, 1177, 1096, 945, 879 cm^{-1}; ^{1}H NMR and ^{13}C NMR data (Table 4); HRESIMS *m/z* 193.1243 $[M + H]^+$ (calcd. for $C_{12}H_{17}O_2$, 193.1229).

Antimicrobial Activity Assay. Compounds **1**, **4**, **5**/**6**, **10**, **15**-**19**, **21**, **23**, and **24** were evaluated for their antimicrobial activities against two bacteria (*Escherichia coli* CGMCC 1.2385, *Staphylococcus aureus* subsp. *aureus* CGMCC 1.2386) and a fungus (*Candida albicans* CGMCC 2.2086), using a paper disk (diameter, 6 mm) assay according to a reported method,[20] with slight modifications. The positive controls were ciprofloxacin and amphotericin B. Petri dishes containing 20 mL of LB agar (for two bacteria) or YPD agar (for fungus) media were seeded with the test strain (1×10^6 cfu/mL). A 5 μL aliquot of each compound (20 mg/mL) was pipetted onto each disk and placed onto the plates which were then incubated overnight at 37 °C. The antimicrobial activities of the compounds were assessed by measuring the diameter of the zone (in mm) of inhibition.

RESULTS AND DISCUSSION

In the current study, a total of 30 terpenoids, including 24 sesquiterpenoids, among which 13 were new, and six triterpenoids were isolated from an ethyl acetate extract of *E. jambolana* seeds using a combination of column chromatography with MCI, silica gel, and Sephadex LH-20 as well as semipreparative HPLC. Their structures were determined on the basis of spectroscopic data analysis and by comparison of these to literature data where available. Among the isolates, **1**−**3**, **5**−**11**, and **13**−**15** were new compounds, named jambolanins A−K and jambolanes A−B, respectively. The structures of the isolated sesquiterpenoids (**1**−**24**) are shown in Figure 1.

Compound **1** was obtained as a colorless oil. A molecular formula of $C_{15}H_{22}O_3$ with five degrees of unsaturation was established on the basis of the HRESIMS and ^{13}C NMR data (Table 1). The IR spectrum exhibited characteristic absorption bands of an α,β-unsaturated ketone moiety (1709, 1645 cm^{-1}),[21] which was confirmed by the ^{13}C NMR data (δ_C 204.0, C-3; δ_C 140.5, C-4; δ_C 164.1, C-5). The ^{1}H and ^{13}C NMR data of **1** (Table 1) were closely related to those of 6β,7β-epoxyguai-4-en-3-one,[22] except for the absence of a methine group along with the appearance of an extra oxygenated quaternary carbon (δ_C 80.5, C-1) in **1**, indicating that compound **1** was the 1-hydroxy derivative of 6β,7β-epoxyguai-4-en-3-one. This conclusion was supported by the obvious β-shifts in the resonance of C-2 (δ_C 50.0 in **1** vs 40.5 in 6β,7β-epoxyguai-4-en-3-one) and C-10 (δ_C 38.9 in **1** vs 32.8 in 6β,7β-epoxyguai-4-en-3-one) and was further confirmed by the observed HMBC correlations from OH-1 (δ_H 4.64) to C-1/C-2/C-5/C-10 (Figure 2).

The relative stereochemistry of chiral centers in **1** was established based on NMR data analysis and NOESY experiment. The high field shifts of carbon and proton resonances associated with the shielded secondary methyl group (δ_H 0.57; δ_C 13.7) suggested it was at a *pseudo*-axial conformation and *trans*-oriented with the hydroxy group at C-1, which was consistent with previous reports.[21,23] This conclusion was supported by the observed NOESY correlations between OH-1 and H-10 (assumed to be α-oriented). In addition, the NOESY correlations of H_3-14 with H_3-12/H_3-15 and H-6 with H-11/H_3-13/H_3-15, and the absence of cross peaks between OH-1 and H-6 suggested the hydroxy group at C-1 and the epoxide ring at C-6 and C-7 were α-oriented, while

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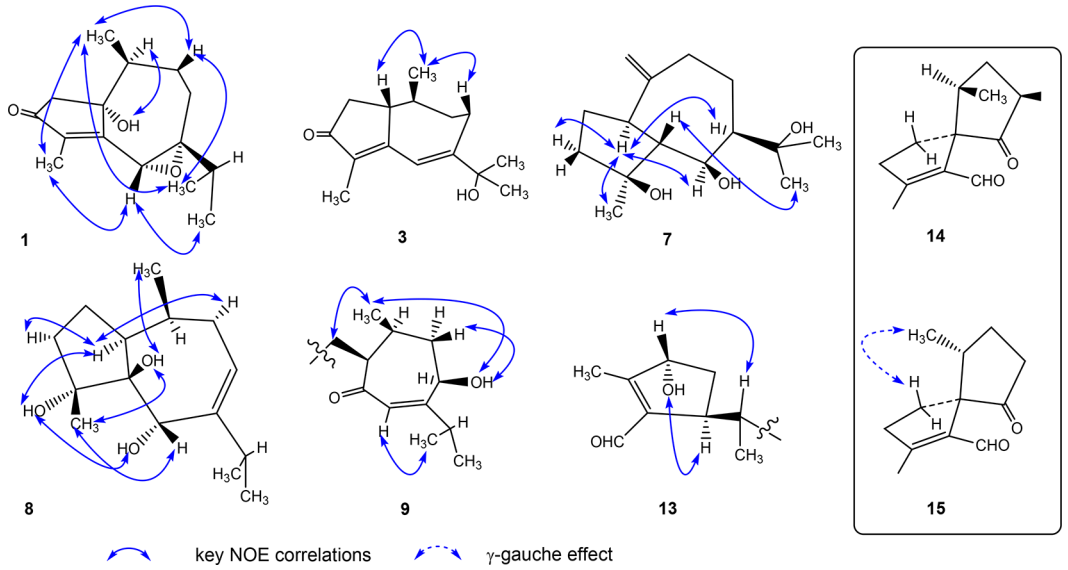

Figure 3. Key NOE correlations of compounds **1**, **3**, **7**–**9**, and **13**, and the steric effects in **15**.

the secondary methyl group and isopropyl group were *β*-oriented (Figure 3). Thus, the structure of **1** was determined to be (1*α*,10*β*)-1-hydroxy-6*α*,7*α*-epoxyguai-4-en-3-one and assigned the trivial name of jambolanin A.

Jambolanin B (**2**), a light yellow oil, was assigned a molecular formula of $C_{15}H_{22}O_2$ on the basis of HRESIMS and ^{13}C NMR data. The UV, IR, and ^1H and ^{13}C NMR spectroscopic data of **2** were similar to those of **1**, indicating that compound **2** was also a guaiane-type sesquiterpenoid derivative. Analysis of the NMR data (Table 1) revealed that the epoxy group in **1** was absent, and instead, a double bond (δ_H 6.12, δ_C 116.5, C-6; δ_C 159.7, C-7) was present in **2** between C-6 and C-7. This observation was confirmed by the HMBC correlation signals from H-6 to C-1/C-4/C-5/C-7/C-8/C-11. The same relative configuration of C-1 and C-10 in **2** as in **1** was established on the chemical shifts of the secondary methyl group (Table 1)[21,23] and observed NOESY correlations of H_3-14 with H-2*β*/H-8*β*/H-9*β* and OH-1 with H-2*α* and H-10. Hence, the structure of **2** was determined as (1*α*,10*β*)-1-hydroxy-4,6-guaiadien-3-one.

The ^1H and ^{13}C NMR spectra of **3** were similar to those of sootepdienone (**4**),[24] a known 4,6-guaiadien-3-one derivative with the same molecular formula. Detailed 2D NMR data analysis revealed that compound **3** had an identical planar structure to that of **4**. Compared to **4**, the chemical shifts of Me-14 in **3** was shifted downfield (δ_H 1.01, δ_C 22.2 in **3** vs δ_H 0.62, δ_C 15.0 in **4**, DMSO-d_6 as solvent), which indicated that the conformation of the secondary Me was changed from *pseudo*-axial in **4** to equatorial in **3**. In this conformation, Me-14 in **3** is less shielded by the carbonyl group at C-3, which is in agreement with previous reports.[21,23] Thus, compound **3** was deduced to be the 1*β*-epimer of **4**. This inference was supported by the correlation signals of H-1 with H_3-14 in the NOESY spectrum. Therefore, the structure of **3** was determined as (1*β*,10*β*)-11-hydroxy-4,6-guaiadien-3-one and named as jambolanin C.

Compounds **5** and **6**, which have the same molecular formula of $C_{15}H_{22}O_2$, were obtained as an inseparable mixture in a nearly 3:2 ratio on the basis of the NMR spectroscopic data analysis. The NMR data of compounds **5** and **6** (Table 2) were almost identical and closely related to those of nardoguaianones J and F,[25] which are a pair of stereoisomers with a 1(5),6-guaiadien-2-one skeleton, indicating **5** and **6** were also stereoisomers with the same structural skeleton. The HMBC correlations from OH-4 (δ_H 5.20 for **5** and 5.18 for **6**) to C-3 (δ_C 51.5 for **5** and 50.8 for **6**), C-4 (δ_C 74.5 for **5** and 74.8 for **6**), and C-5 (δ_C 165.7 for **5** and 165.9 for **6**), and from H-10 (δ_H 2.80 for both **5** and **6**) to Me-14 (δ_C 19.6 for **5** and 19.9 for **6**) and C-5 revealed that the hydroxy group was located on C-4 in both compounds **5** and **6**, instead of on C-10 in nardoguaianones J and F. Considering that biogenetically all plant-derived guaianoids bear a 4*α*-methyl orientation,[25] the structures of jambolanins E (**5**) and F (**6**) were proposed to be (4*α*,10*α*)-4-hydroxy-1(5),6-guaiadien-2-one and (4*α*,10*β*)-4-hydroxy-1(5),6-guaiadien-2-one, respectively.

Compound **7** was assigned the molecular formula $C_{15}H_{26}O_3$ on the basis of HRESIMS and ^{13}C NMR data. Its IR spectrum showed absorptions of a hydroxy group (3381 cm^{-1}) and an olefinic bond (1639 cm^{-1}). The NMR spectra of **7** revealed the presence of an exomethylene group, three tertiary methyl groups, one oxygenated methine, and two oxygen-bearing quaternary carbons. Compound **7** possessed the same molecular formula and similar IR and NMR data (Table 2) as those of 4*α*,7*β*,11-trihydroxy-1*βH*,5*αH*-guai-10(14)-ene.[26] The major difference between the two compounds was the replacement of an oxygenated quaternary carbon and a methylene group in **4** with an oxygenated tertiary carbon (δ_H 4.11; δ_C 70.4) and a methine (δ_H 1.42; δ_C 51.0) in **7**, suggesting the location change of one hydroxy group. The hydroxy group in **7** was located on C-6, based on HMBC correlations from H-1 to C-2/C-5/C-6 and from H_3-15 to C-3/C-4/C-5. The above spectroscopic evidence led to the proposal of the planar structure of 4,6,11-trihydroxy-guai-10(14)-ene for **7**. H-5 was assigned a *β*-axial orientation based on the coupling constant value between H-1 (*α*-orientation) and H-5 ($J_{1,5}$ = 11.0 Hz) and the absence of cross-peaks between H-1 and H-5 in the NOESY spectrum. Furthermore, the observed NOESY correlations of H-1 with H-6/H-7/H_3-15 indicated their *cis*-orientation. Thus, compound **7** was elucidated as 4*β*,6*β*,11-trihydroxy-1*αH*,5*βH*,7*αH*-guai-10(14)-ene and named jambolanin F.

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Compound **8** was determined to have the same molecular formulas as **7** on the basis of HRESIMS (509.3839 $[2M+H]^+$, calcd. 509.3842) and ^{13}C NMR data. Comparison of the ^1H and ^{13}C NMR data between compounds **7** and **8** (Table 2) suggested that **8** was also a guaiane-type sesquiterpene. The HMBC correlation signals from H-6 to C-4/C-5/C-7/C-8/C-11 indicated that the location of the olefinic bond in **8** was different from compound **7**. Moreover, the HMBC correlation signals from H_3-15 to C-3/C-4/C-5 suggested that the hydroxy group substituted at C-11 in **7** was present on C-5 in compound **8**, which was supported by the doublet peaks of two isopropyl methyls (δ_H 1.00, d, J = 6.7 Hz, H_3-12; δ_H 0.98, d, J = 6.7 Hz, H_3-13). The NOESY correlations of H-1 (α-oriented) with H-3α/H-9α/OH-4/OH-6 and the absence of cross peaks from H-1 to H-6/H_3-14/H_3-15 indicated OH-4 and OH-6 were α-oriented while Me-14 and Me-15 were β-oriented. Furthermore, observed NOESY correlations of OH-5 with H-6/H_3-14/H_3-15 implied their *cis*-orientation. Consequently, the structure of **8** was determined to be 4α,5β,6α-trihydroxy-guai-7-ene and named as jambolanin G.

Jambolanin H (**9**) possessed a molecular formula of $C_{15}H_{24}O_3$, as determined by the HRESIMS ion at m/z 253.1851 ($[M + H]^+$). The UV, IR and NMR spectroscopic data of **9** were quite similar to those of gibberodione (**12**),[27] a 4,5-*seco*-guaiane with a 3-oxobutyl side chain, except that a sp^3 methylene (δ_H 2.16, 2.33; δ_C 29.6) in **12** was replaced by an oxygenated sp^3 methine (δ_H 4.30; δ_C 68.2) in **9**. The HMBC correlations from H-8 to C-6/C-7/C-9/C-10/C-11 and the $^1H-^1H$ COSY correlation between H-8 and OH-8 revealed an extra hydroxy group was located on C-8. The NOESY correlations (Figure 3) and the similarly upfield chemical shifts of H_3-14 (δ_H 0.74; δ_C 16.9) suggested **9** has the same *Z*-configured 6,7-double bond and same relative configuration (1αH,10αH) of H-1 and H-10 as those of **12**.[27] OH-8 was determined to be *cis*-oriented to the secondary methyl group based on its correlation signals with H_3-14 in the NOESY spectrum. Thus, the structure of jambolanin H (**9**) was assigned as (1αH,10αH)-8β-hydroxy-4,5-*seco*-guai-6-ene-4,5-dione.

The molecular formulas of compounds **10** and **11** were the same as that of **9**, as indicated by HRESIMS data. The close similarity of the UV, IR, and NMR spectroscopic data of **10** and **11** with those of **9** indicated both **10** and **11** to be homologues of **9**. Compared to **9**, the presence of an oxygenated quaternary carbon (δ_C 72.6 in **10** and 71.3 in **11**) instead of a tertiary carbon, and the significant downfield shift of isopropyl methyl groups (around 6 ppm) revealed the hydroxy group was transferred from C-8 in **9** to C-11 in both **10** and **11**. This conclusion was supported by HMBC correlations from OH-11 to C-7/C-12/C-13 in **10** and **11**, respectively. Thus, compounds **10** and **11** were identified as stereoisomers with the planar structure 11-hydroxy-4,5-*seco*-guai-6-ene-4,5-dione. By further inspection of the NMR data of **10** and **11**, the obvious difference of chemical shifts of the secondary methyl group (δ_H 0.67; δ_C 16.5 in **10** vs δ_H 1.04; δ_C 19.1 in **11**) enabled the assignment of relative configuration for **10** and **11** as 1αH,10αH and 1βH,10αH, respectively.[27] Consequently, the structures of compounds **10** and **11** were determined as shown and named as jambolanins I and J, respectively.

The molecular formula of jambolanin K (**13**) was established as $C_{15}H_{24}O_3$ by HRESIMS data. The IR spectrum exhibited absorption bands of hydroxyl (3433 cm^{-1}), carbonyl (1708 cm^{-1}), and olefinic (1667 cm^{-1}) functionalities. The ^{13}C NMR spectrum of **13** displayed 15 carbon signals assigned to two carbonyls, two quaternary olefinic carbons, four methines (including one oxygenated carbon at δ_C 78.9), three methylenes, and four methyls (including one vinyl methyl). As depicted in Figure 2, the HMBC correlation signals from H_3-12/H_3-13/H_2-8 to the ketone carbon at δ_C 214.4 in conjunction with $^1H-^1H$ COSY correlation signals revealed the presence of a 2,6-dimethyl-3-oxoheptyl group. The observed HMBC correlations from the olefinic methyl (H_3-15) to C-3/C-4/C-5 and from the aldehyde proton (H-6) to C-1/C-5 allowed the establishment of the 3-hydroxyl-4-methyl-5-formyl-cyclopentene moiety with the aid of $^1H-^1H$ COSY spectroscopic analyses. Finally, the correlation of H_3-14 with C-1/C-9/C-10 indicated the linkage of the cyclopentene moiety and side chain through C-1/C-10. Thus, the planar structure of **13**, with a rare 6,7-*seco*-guaiene skeleton, was established. The NOE interactions of H-1 with OH-3 suggested H-1 and OH-3 were *cis*-oriented. Based on the aforementioned evidence, the structure of jambolanin K (**13**) was determined as (1αH,3βH)-1-[(2,6-dimethyl-3-oxo)-2]-heptyl-3-hydroxyl-4-methyl-5-formyl-1-cyclopentene.

Compound **14** was determined to have the molecular formula $C_{12}H_{16}O_2$ with four degrees of unsaturation on the basis of HRESIMS and ^{13}C NMR data. The IR spectrum suggested the presence of carbonyl (1731 cm^{-1}) and olefinic (1669 cm^{-1}) functionalities. The NMR data of **14** (Table 4) suggested the presence of a nonconjugated ketone group (δ_C 221.5), an aldehyde group (δ_H 9.81, s; δ_C 188.5), a secondary methyl (δ_H 0.83, J = 7.1 Hz; δ_C 16.7), and an olefinic methyl (δ_H 2.20; δ_C 15.2). The ^{13}C NMR spectrum of **14** displayed all the carbon signals (Table 4) indicated by the molecular formula. $^1H-^1H$ COSY analyses indicated the presence of two spin systems (H_2-6/H_2-7 and H_2-2/H_2-3/H-4/H_3-10). The HMBC correlations from H_2-2 and H-3β to the ketone carbon (C-1) and from H_3-10 to C-3/C-4/C-5 established fragment I (Figure 2). Similarly, the HMBC correlations from H_3-12 to C-7/C-8/C-9 and from the aldehyde proton (H-11) to C-5/C-8/C-9 established fragment II (Figure 2). Finally, the HMBC correlations of H-6β (δ_H 2.11) with C-1/C-4/C-5 indicated the linkage of fragment I and II through C-5. Thus, the planar structure of **14** with a spiro[4.4]nonane skeleton was established.

Compound **15** was determined to have the same molecular formula as **14** on the basis of HRESIMS and ^{13}C NMR data. Detailed 2D NMR analysis revealed that compound **15** had a planar structure identical to that of **14**. Compared with **14**, the carbon resonances of C-4 and C-6 (Table 4) in **15** were obviously shifted upfield arising from the steric effects (γ-gauche effect) caused by the axial-oriented methyl substituent at C-4 (Figure 3), which indicated that compounds **14** and **15** were a pair of diastereoisomers and the secondary methyl at C-4 in **15** was β-oriented, while α-oriented in **14**. Hence, the relative sterostructures of jambolanes A (**14**) and B (**15**) were determined as *rel*-4*S*,5*R*-4-methyl-6-formylspiro[4.4]non-6-ene-1-one and *rel*-4*R*,5*R*-4-methyl-6-formylspiro[4.4]non-6-ene-1-one, respectively.

Apart from jambolanins A–K and jambolanes A and B, 11 known sesquiterpenoids, including sootepdienone (**4**),[24] gibberodione (**12**),[27] orientalol E (**16**),[28] guaianediol (**17**),[29] junipediol (**18**),[30] cryptomeridiol (**19**),[31] litseachromolaevanes A (**20**),[32] (4*R*)-4-hydroxy-1,10-*seco*-muurol-5-ene-1,10-dione (**21**),[33] (8*R*,9*R*)-isocaryolane-8,9-diol (**22**),[34] and caryolandiol (**23**),[35] clovane-2β,9α-diol (**24**),[36] along with six known triterpenoids, actinidic acid (**25**),[37] oleanolic acid (**26**),[38]

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ursolic acid (**27**),[39] corosolic acid (**28**),[40] arjunolic acid (**29**),[41] and asiatic acid (**30**),[40] were isolated and identified from the ethyl acetate extract of *E. jambolana* seeds. In the current study, the majority of the isolated sesquiterpenoids were of the guaiane type, one compound (**13**) possessed a rare 6,7-*seco*-guaiene skeleton, and two compounds (**14** and **15**) were norsesquiterpenoids with a spiro[4.4]nonane skeleton. All of the sesquiterpenoids except compounds **19**,[42] **23**, and **24**[43] are being reported from the Myrtaceae family for the first time.

E. jambolana has been used in folk medicine to treat infection related diseases,[2,3] and the essential oil of this plant had been reported to possess antimicrobial properties against *Staphylococcus aureus* and *Escherichia coli*.[13] Thus, in the current study, the sesquiterpenoids which were isolated in adequate quantities (>2 mg) were evaluated for their antimicrobial activities against the Gram-positive bacterium *Staphylococcus aureus*, Gram-negative bacterium, *Escherichia coli*, and the fungus *Candida albicans*, respectively. As shown in Table 5, the

Table 5. Antibacterial Activity against *Staphylococcus aureus* of Some Sesquiterpenoids Isolated from *E. jambolana* Seeds

Compound	Amount (μg/disk)	inhibitory zone diameter (mm)
1	100	
5/6	100	10 ± 0.9
10	100	
15	100	
4	100	9 ± 0.5
16	100	
17	100	9 ± 0.4
18	100	
19	100	8 ± 0.3
21	100	7 ± 0.2
23	100	9 ± 0.4
24	100	10 ± 0.8
ciprofloxacin[a]	5	24 ± 1.1

[a]Positive control substance.

mixture of new compounds **5/6** (100 μg/disk) showed mild inhibition on the proliferation of *S. aureus* with inhibitory zone diameters of 10 mm. The known compounds **4**, **17**, **19**, **21**, **23**, and **24** also displayed antimicrobial activity against *S. aureus*. None of the tested compounds were active against *E. coli* and *C. albicans* at the concentration 100 μg/disk. Caryolandiol (**23**) has been reported to possess antimicrobial activity against *S. aureus*,[20] which is consistent with our result. To the best of our knowledge, this is the first report regarding the antimicrobial activity of the known sesqutierepenoids sootepdienone (**4**), guianediol (**17**), cryptomeridiol (**19**), (4*R*)-4-hydroxy-1,10-*seco*-muurol-5-ene-1,10-dione (**21**), and clovane-2β,9α-diol (**24**).

In summary, 30 terpenoids were isolated and identified from *E. jambolana* seeds. Among these, 13 were new sesquiterpenoids (**1**−**3**, **5**−**11**, and **13**−**15**), and twenty-one compounds (**1**−**18**, **20**−**22**) are identified from the Myrtaceae family for the first time. The antimicrobial activities exhibited by some of the isolates suggest that sesquiterpenoids may partially contribute to the effects against infection related diseases attributed to this plant, but further research using in vivo models would be required to confirm this. The results reported here advance current scientific knowledge of *E. jambolana* and confirm that this food-derived plant contains a wide diversity of bioactive phytochemicals supporting its nutraceutical and functional food applications.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.jafc.7b04066.

IR, HRMS, and NMR spectra of compounds **1**−**3**, **5**−**11**, and **13**−**15** (PDF)

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Notes

The authors declare no competing financial interest.

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