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RESEARCH ARTICLE

Characterization of New Lignan and alcohol from the water extract of *Ipomoea cairica*

***Shaista Naz, Sumayya Saied, Erum Zahir and Humaira Siddiqi**
Department of Chemistry, University of Karachi, Pakistan

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Corresponding Author

Dr. ShaistaNaz

Abstract

New lignans and alcohols were isolated from the water extractof *Ipomoeacairica*, after hydrodistillation of leaves for the exctaction of essential oils. Their molecular structures were determined on the basis of spectral analysis including UV, IR, MS, ^{13}CNMR and 2D-NMRspectroscopy.**Diarctigeninol (1)** and **4-(3′,5′-Dimethoxy phenyl) -2-methyl -1-butanol (3)**werefound benew compounds**.Gnidifolin (2)** was isolatedas a new source.

INTRODUCTION

Ipomoea cairica (L.)Sweetis a specie of morning glory and commonly known as railroad creeper. It has funnel-shaped mauve-pink to purplish flowers. It can flower all year round. It is found in tropical and sub-tropical regions as herbs, climbers, or shrubs. The natural products reported in the species of this family may be classified as polyketides, terpenoids, steroids, shikimides (coumarins,benzoic and cinnamic acid derivatives), flavonoids and alkaloids [Olga O. de A. Lima and RaimundoBraz-Filho**1997**].It is used in Brazilian folk medicine for the treatment of rheumatism and inflammations.It is also used for treating cough and asthma, acute and chronic viral hepatitis type B, liver cirrhosis, jaundice, innominate toxic swelling, and breast carcinoma [Rastogi R. P., Mehrotra B. N., (2001)(Rong-Jyh Lin., Chung-YiChen.,. Wen-LiLo, 2008)] Lignans isolated from *Ipomoea cairica* have proved to be appealing compounds as potential antitumor, anti HIV and Ca^{2+} antagonist agents. [Pàska C., et al.,1999]. Our present work was based on the isolation and characterization of lignans and essential oils.

Materials and method

The fresh aerial parts (500g) of plant were hydrodistilled in a Clevenger-type apparatus for 5hrs. The distillate was extracted with dichloromethane; the solvent layer was dried over anhydrous sodium sulphate and concentrated on rotatory evaporator. The yield of the oil was found to be 0.85g (0.17%).
After hydrodistallationthe remaining water extract of the plant was further extracted thrice with ethylacetate. The ethylacetate layer was concentrated on rotatory evaporator yielding 0.8g of residue. It was purified on preparative TLC plates (20×20 cm), (chloroform-methanol, 9:1 eluted) yielding four pure compounds, **Diarctigeninol (1)** 20 mg**, Gnidifolin (2)** 10 mg**, 4-(3′,5′-dimethoxy phenyl)-2-methyl-1-butanol (3)** 15 mg**,** and**Arctigenin (4)** 15mg,

Results

Diarctigeninol (1)

White solid (yield 20 mg).**Rf**: 0.65 ($CHCl_3$:MeOH :: 9 : 1). **UV ($CHCl_3$) λ_{max} nm:** 282, 240.**IR ν_{max} cm^{-1}:** 1745, 3445, 1630. **HR-FAB-MS (pos) *m/z* :**759.29971$[M+H]^+$ (Calcd, for C_{42} H_{47} O_{13}, 759.30171).**EIMS *m/z* (rel. int. %) :** 387 (6.9), 371 (5.1), 167 (20.5), 151 (13.2), 137 (100). For ^{13}C-NMR and ^{1}H-NMR see table:1

Gnidifolin (2)

White solid (yield 10 mg).**Rf**: 0.61 ($CHCl_3$:MeOH :: 9 : 1). **UV ($CHCl_3$) λ_{max} nm:** 284 **IR ν_{max} cm^{-1}:** 1748, 3440 , 1600, 1484. **HR-EIMS *m/z*:** 374.13250 (Calcd. for $C_{20}H_{22}O_7$,374.13656). **EIMS *m/z* (rel. int. %) :** 374 $[M^+]$ (5), 314 (8.5), 237 (4.75), 137 (100), 139 (9.5), 153 (7.2), 84 (51).For ^{13}C-NMR and ^{1}H-NMR see table:1

4-(3′.5′-Dimethoxy phenyl) -2-methyl -1-butanol (3).

White crystals (yield 15 mg). **Rf:** 0.559 ($CHCl_3$:MeOH :: 9 : 1). **HR-EIMS *m/z*:** 224.1398 (Calcd. for $C_{13}H_{20}O_3$,224.1413). **EIMS *m/z* (rel. int. %):** 224 (M^+, 2.1), 206 (2.5), 194 (3.21), 163 (3.3), 151 (3.21), 137 (100), 87 (14.1).For ^{13}C-NMR and ^{1}H-NMR see table:1

Arctigenin (4)

White solid (yield 15 mg).**Rf**: 0.7 ($CHCl_3$: MeOH :: 9 : 1). **UV ($CHCl_3$) λ_{max} nm:** 282.
IR ν_{max} cm^{-1}: 1735, 3440, 1580. **HR-EIMS *m/z*:** 372.1462 (Calcd. for $C_{21}H_{24}O_6$,372.15732). **EIMS *m/z* (rel. int. %) :** 372 $[M^+]$ (3), 314 (8.9), 249 (9.1), 151 (11.3), 137 (25.4), 123 (13.6), 121 (5.7), 84 (8.2). For ^{13}C-NMR and ^{1}H-NMR see table:1

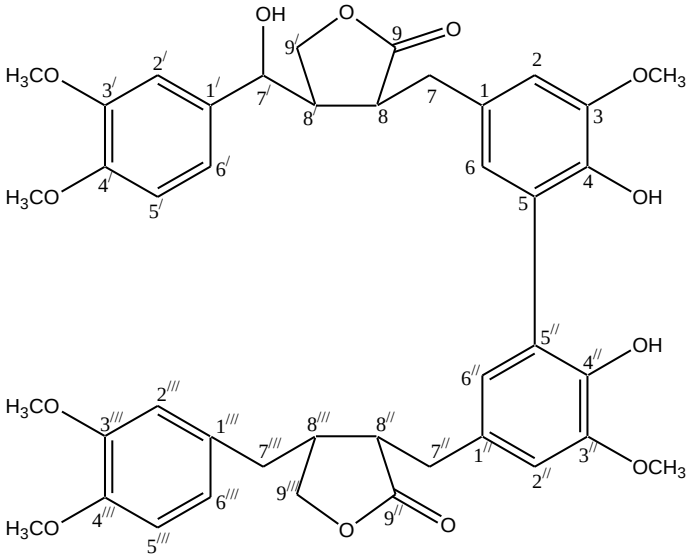
Myristyl alcohol (1- Tetradecanol) (5)

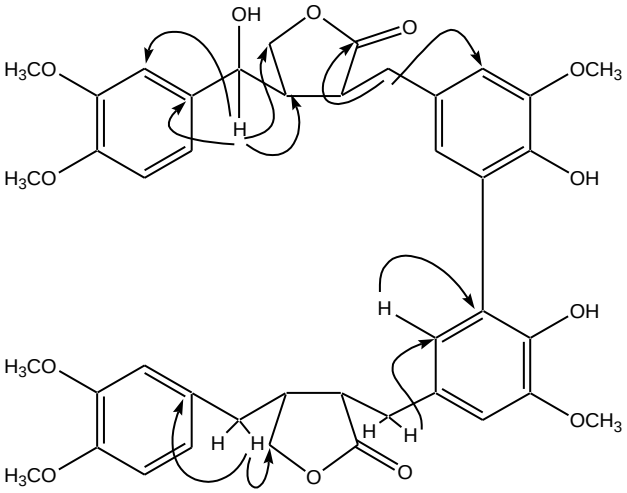
White crystals (yield 80 mg). **Rf:** 0.55 (Hexane: EtOAc : 8 : 2). **EIMS *m/z* (rel. int. %): 2**14 (M^+, 2.75), 197 (1.34), 183 (1.42), 169 (1.73), 155 (2.29), 127 (4.08), 99(10.5), 85 (24.53), 57 (100).**[1] H-NMR (CD_3OD, 300 MHz) δ:** 4.11 (2H, dd, *J* = 6.9, 6.5 Hz), 1.303 (2H, m, CH_2), 0.86 (3H, t, *J* = 7.2 Hz, CH_3).**^{13}C-NMR (CD_3OD, 75 MHz) δ:** 62.5 **(**C-1), 32.1(C-2), 31.9 (C-12), 29.9 (C-5), 29.7 (C-11), 29.6 (C-7, 9), 29.5(C-6,10), 27.3(C-4), 24.5 (C-3), 22.7 (C-13), 14.2 (C-14).

Table 1 :^{13}C and ^{1}H NMR spectral data of compounds 1–3 ($CDCl_3$,(δ) in ppm, *J* in Hz)

	1		**2**		**3**	
Position	(δ)^{13}C	(δ)^{1}H	(δ) ^{13}C	(δ) ^{1}H	(δ)^{13}C	(δ)^{1}H
1	147.7	-	119.1	-	60.9	3.76 (m)
2	112.0	6.38 (d, *J* = 1.8)	144.3	-	43.8	2.31(m)
3	149.6	-	134.9	-	29.3	2.31(m)
4	144.6	-	148.4	-	35.9	2.72 (t, *J* = 8.1)
5	129.8	-	108.3	6.81 (d, *J* = 8.0)	-	-
6	123.1	6.44 (d, *J* =1.8)	127.1	6.84 (d, *J* = 8.0)	-	-
7	38.6	a 2.47(dd,*J*= 15.0, 8.7) b 2.58 (dd, *J* = 15.0, 7.8)	28.1	2.92 (d, *J* = 7.2)	-	-
8	46.4	2.40 (brs)	47.7	2.51 (td, *J* = 7.2, 5.6)	-	-
9	178.3	-	178.5	-	-	-
1′	130.1	-	129.3	-	132.4	-
2′	108.6	6.38 (d, *J* = 1.8)	110.9	6.60 (s)	114.1	6.62 (d, *J* = 1.8)
3′	146.7	-	146.3	-	142.1	-
4′	145.0	-	144.6	-	121.7	6.60 (d, *J* = 1.8)
5′	111.9	6.73 (d, *J* = 8.4)	113.8	6.69 (d, *J* = 8.8)	156.9	-
6′	120.8	6.78 (dd, *J* = 8.1, 1.8)	121.7	6.86 (dd, *J* = 8.0, 1.8)	113.3	6.56 (d, *J* = 1.8)
7′	85.0	4.70 (d, *J* = 5.4)	37.4	2.50 (m)	-	-
8′	40.0	3.7 (m)	40.3	2.50 (m)	-	-
9′	71.7	4.23(dd,*J* = 9.0, 6.9 H-9a) 4.25(dd,*J* = 8.8, 6.9, H-9b)	71.7	3.83 (dd, *J* = 8.8, 7.6)	-	-
1″	147.6	-	-	-	-	-

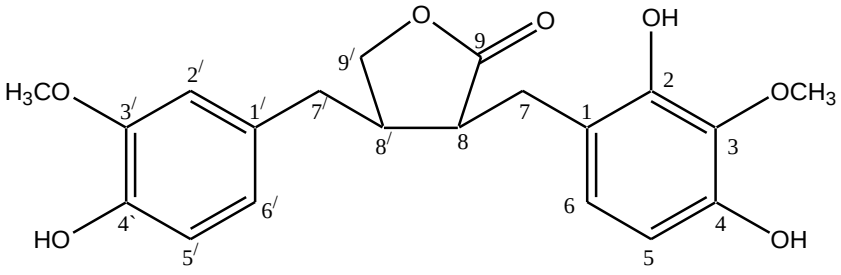
$2''$	114.2	6.47 (d, *J* =1.8)	-	-	-	-
$3''$	149.4	-	-	-	-	-
$4''$	144.6	-	-	-	-	-
$5''$	129.7	-	-	-	-	-
$6''$	122.9	6.61 (d, *J* =1.8)	-	-	-	-
$7''$	42.2	2.9 (dd, *J* = 14.0, 7.7)	-	-	-	-
$8''$	46.9	2.42 (br s)	-	-	-	-
$9''$	178.8	-	-	-	-	-
$1'''$	130.0	-	-	-	-	-
$2'''$	114.3	6.50 (d, *J* = 1.8)	-	-	-	-
$3'''$	148.9	-	-	-	-	-
$4'''$	149.5	-	-	-	-	-
$5'''$	112.6	6.88 (d, *J* = 6.6)	-	-	-	-
$6'''$	120.5	6.68 (dd, *J* = 6, 1.8)	-	-	-	-
$7'''$	34.8	3.09 (dd, *J* =13.8, 7.7) 2.93 (dd, *J* =13.5, 7.9)	-	-	-	-
$8'''$	40.1	2.50 (m)	-	-	-	-
$9'''$a $9'''$b	71.4	a 3.94 (dd, *J* = 8.9, 3.3) b 3.96 (dd, *J* = 8.9, 3.9)	-	-	-	-
OCH_3	55.9	3.89 (s, C-$3'$)	56.3	3.62 (s, C-$3'$)	55.9	3.79 (s, C-$3'$)
OCH_3	55.8	3.84 (s, C-$4'$)	55.5	3.70 (s, C-3)	55.9	3.79 (s, C-$5'$)
OCH_3	55.7	3.79 (s, C-3)	-	-	-	-
OCH_3	54.2	3.83 (s, C-$3'''$)	-	-	-	-
OCH_3	56.1	3.92 (s, C-$4'''$)	-	-	-	-
OCH_3	55.8	3.78 (s, -$3''$)	-	-	-	-
CH_3	-	-	-	-	14.1	0.85 (m)



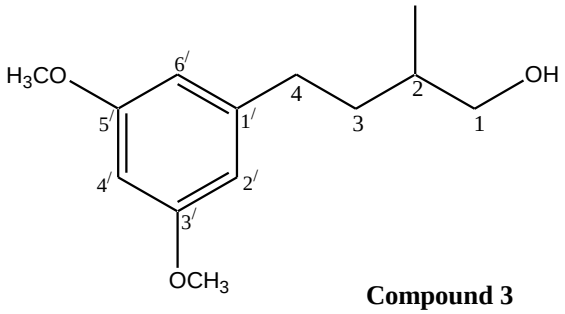


Compound 1

Important HMBC correlations



Compound 2



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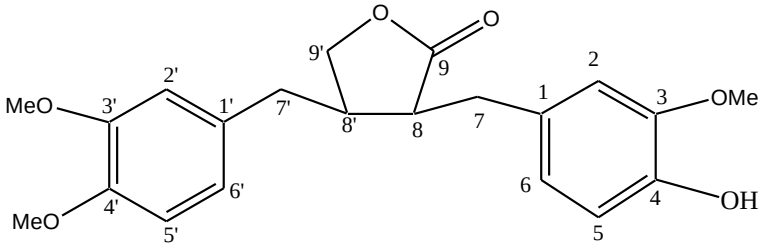

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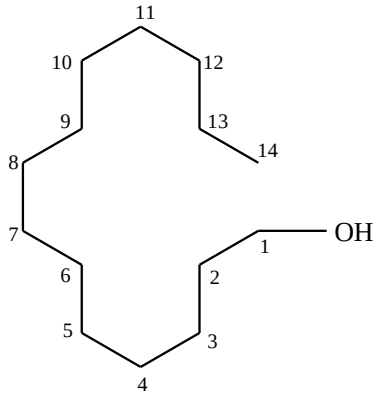

Compound 5

Discussion

Diarctigeninol (1)

The compound **119** was obtained as pale yellow solid. The molecular formula $C_{42}H_{46}O_{13}$ was deduced from the HR-FAB-MS (Positive) which showed $[M+H]^+$ ion at *m/z* 759.29971 (calculated for C_{42} H_{47} O_{13}). The EI-mass spectrum showed fragments at m/z 387 $[M - C_{21}H_{23}O_6]^+$ and 371 $[M - C_{21}H_{23}O_7]^+$ corroborated the cleavage of two

monomeric units that forms the dimer(a dilignan). The other important peaks were observed at *m/z* 167 [M – C_{33} H_{35} O_{10}]$^+$, and 151 [M – C_{33} H_{35} O_{11}]$^+$ which confirmed the presence of a hydroxyl group in one moiety of arctigenin. IR spectrum showed significant peaks of lactone at 1745 cm^{-1}, hydroxyl group at 3445 cm^{-1} and aromatic nucleus at 1630 cm^{-1}.

The ^{1}H-NMR exhibited four *meta* coupled doublets at δ 6.38 (H-2$^{/}$), 6.44 (H-6), 6.47 (H-2$^{//}$), and 6.61 (H-6$^{//}$). Two ABX coupling systems existed through the signals at δ 6.78 (1H, dd, J = 8.1, 1.8 Hz, H-6$^{/}$), 6.73 (1H, d, J = 8.4 Hz, H-5$^{/}$), 6.38 (1H, d, J = 1.8 Hz, H-2$^{/}$), and 6.68 (1H, dd, J = 6, 1.8 Hz, H-6$^{///}$), 6.88 (1H, d, J = 6.6 Hz, H-5$^{///}$), and 6.50 (1H, d, J = 1.8 Hz, H-2$^{///}$). Six singlets at δ 3.89, 3.84, 3.79, 3.83, 3.78 and 3.94 corroborated the presence of six methoxy groups in the molecule. Furthermore, ^{1}H-NMR showed a doublet at δ 4.70 indicating the presence of an oxymethine proton. Five double doublets appeared at δ 4.23 (H_2-9$^{/}$), 2.47 (H_2-7), 3.09 (H_2-7$^{///}$), 3.94 (H_2-9$^{///}$) and 2.90 (H_2-7$^{//}$) were attributable to methylene groups.The^{1}H - ^{13}C HMBC spectrum showed long range correlations between 4.70 (H-7$^{/}$) and 108.6 (C-2$^{/}$), 120.8 (C-6$^{/}$), 40.0 (C-8$^{/}$) and 71.7 (C-9$^{/}$) and the other one between δ 2.47 (H_2-7) and 178.3 (C-9) and 112.0 (C-2$^{/}$). These correlations signified that the oxymethine group is attached to one moiety of arctigenin at C-7. From all these assignments and comparison with the literature survey [(Olga O. de A. Lima **1997)**(Kim BH.and et al., (2008)(Rong-Jyh Lin., and et al., 2008)], it was concluded that the compound **1** is a dimer of arctigenin with a hydroxyl group at C-7. It was named as **diarctigeninol (**4$^{/}$,7$^{/}$-dihydroxy-3,3$^{/}$,4$^{/}$-trimethoxyligano-[5,5$^{//}$-biphenyl]-4$^{//}$-hydroxy-3$^{//}$,3$^{///}$,4$^{///}$-trimethoxyligano-9,9$^{/}$:9$^{//}$,9$^{///}$-dilactone).

Gnidifolin (2)

Compound**2** was isolated as a white solid and the molecular formula was determined to be $C_{20}H_{22}O_7$ from the molecular ion peak at *m/z* 374.13250 obtained in the HR-EIMS. In the EIMS, the important peaks were observed at *m/z* 314 [M - 2 OCH_3]$^+$, 237 [M – $C_8H_9O_2$]$^+$, 137 [M – $C_{12}H_{13}O_5$]$^+$, 139 [M – $C_{13}H_{15}O_4$]$^+$, 84 [M – $C_{16}H_{18}O_5$]$^+$. The IR spectrum was consistent with the presence of a lactone carbonyl (1748 cm^{-1}), hydroxyl group (3440 cm-1) and aromatic nucleus (1600 cm^{-1}).The ^{1}H and ^{13}C-NMR data and the HMQC spectra provided evidence that **2** possessed two methoxy, five aromatic methine, three methylene, two exomethine, one carbonyl and seven quarternary carbons. The ^{1}H-NMR spectrum of compound **2** revealed the characteristic signals of 1,3,4 trisubstituted aromatic ring at δ 6.69 (1H, d, J = 8.8 Hz), 6.86 (1H, dd, J = 8.0, 1.8), 6.60 (1H , s,) and a 1,2,3,4 tetrasubstituted aromatic ring showing AB doublet at δ 6.81 and 6.84 (J = 8.0 Hz). A double doublet at δ 3.83 corroborated the presence of an oxygenated methylene group. Two singlets at δ 3.62 and 3.70 indicated the presence of two methoxy groups in the molecule. In the light of the above spectral evidences and comparative literature survey [R. F. Bryan and M.-S.Shen**,** (1978)(Rong-Jyh Lin., Chung-YiChen.,. Wen-LiLo,2008)] the structure of compound **2** was concluded to be 2,4,4$^{/}$-trihydroxy-3,3$^{/}$-dimethoxyligano-9,9$^{/}$ lactone (**gnidifolin**).

4-(3$^{/}$,5$^{/}$-Dimethoxy phenyl) -2-methyl -1-butanol (3).

Compound **3** was isolated as white solid from ethyl acetate fraction. The molecular formula $C_{13}H_{20}O_3$ was established by the analysis of HR-EIMS. In the EIMS, compound **3,** furnished ions at *m/z* 224 [M]$^+$, 206 [M – H_2O]$^+$, 193 [M – OCH_3]$^+$ and a base peak at 137 [M – $C_5H_{11}O$]$^+$. The ^{1}H-NMR spectrum showed 3 doublets at δ6.62, 6.60 and 6.56 (J =1.8 Hz), indicating the presence *meta* coupled H's. The coupling constants of these hydrogens indicated that the substituents are present at 3 and 5 positions of the benzene ring. A singlet of 6H at δ 3.79 corroborated the presence of two methoxy groups in the aromatic ring. A multiplet at δ 3.76 indicated the presence of terminal oxymethylene group.

The ^{13}C-NMR corroborated thirteen carbon signals. The multiplicity of the carbon signals was established by carrying out BB and DEPT experiments which indicated the presence of two methoxy, two methylene, one oxymethylene, four methine and three quaternary carbons.In the light of the above spectral evidences the structure of compound **3**was concluded as **4-(3$^{/}$,5$^{/}$-dimethoxy phenyl) -2-methyl -1-butanol**.

Arctigenin (4)

Compound **4** was isolated as white solid. The molecular formula was established as $C_{21}H_{24}O_6$ from HR-EIMS data at *m/z* 372.1462. The other prominent peaks were observed at *m/z* 314 [M- 2 OCH_3]$^+$, 137 [M- $C_{12}H_{15}O_4$]$^+$, 123 [M- $C_{14}H_{17}O_2$]$^+$, 84 [M- $C_{17}H_{20}O_4$]$^+$. Strong IR absorption bands at 3440, 1750 and 1580 cm^{-1} corroborated the presence of hydroxyl group, lactonic carbonyl and aromatic nucleus respectively.

The ^{1}H and ^{13}C-NMR data and the HMQC spectra revealed the presence of three methoxy, six methine, three exomethylene, two exomethine, one carbonyl and six quarternary carbons. The ^{1}H- NMR spectrum showed the characteristic signals of the two sets of 1,3,4-trisubstituted aromatic ring protons at δ 6.44 (1H, d, J = 1.8 Hz, H-2$^{/}$), 6.72 (1H, d, J = 8.4 Hz, H-5$^{/}$), 6.52 (1H, dd, J = 8.0, 1.8 Hz, H-6$^{/}$) and 6.61 (1H , d, J = 1.6 Hz, H-2), 6.79 (1H, d, J = 8.0Hz, H-5), 6.59 (1H, dd, J = 8.1, 1.7 Hz, H-6).
The physical and spectral data was in complete agreement to those reported in literature [Rong-Jyh Lin., Chung-YiChen.,. Wen-LiLo,2008] for 4-hydroxy-3,3$^{/}$,4$^{/}$-trimethoxyligano-9,9$^{/}$-lactone **(Arctigenin)**

Myristyl alcohol (1-Tetradecanol) (5)
Compound **5** was isolated as white crystalline solid and the molecular formula was proposed as $C_{14}H_{30}O$ based on HR-EIMS showing an ion at *m/z* 214.21691 (calculated for 214.22980). The diagnostic fragments occurred at *m/z* 197 $(M - OH)^{+}$, 155 $[M - C_3 H_7 O]^{+}$, 85 $[M - C_8 H_{17} O]^{+}$.The ^{13}C-NMR spectrum (BB and DEPT) revealed the presence of one methyl and thirteen methylene groups.The ^{1}H-NMR spectrum showed a triplet at δ 0.86 (J = 7.2 Hz), a multiplet at δ 1.303 and a double doublet at δ 4.11 (J = 6.9, 9.5 Hz) revealing that it is a straight chain fatty alcohol.
On the basis of above evidences and reported literature [PàskaC.and et al.,(1999)], compound **5** was identified as myristylalcohol.v

References

BryanR. F. and ShenM.-S., **(1978)** Gnidifolin [*trans*-2-(2,4-dihydroxy-3-methoxybenzyl)-3-(4'-hydroxy-3'-methoxybenzyl)butyrolactone] , ActaCryst. B34, 327-329

Kim BH[1], Hong SS, Kwon SW, Lee HY, Sung H, Lee IJ, Hwang BY, Song S, Lee CK, Chung D, Ahn B, Nam SY, Han SB, Kim Y (2008)Diarctigenin, a lignan constituent from Arctiumlappa, down-regulated zymosan-induced transcription of inflammatory genes through suppression of DNA binding ability of nuclear factor-kappaB in macrophages.JPharmacol.ExpTher. 327(2):393-401.

Olga O. de A. Lima and RaimundoBraz-Filho(1997)DibenzylbutyrolactoneLignans and Coumarins from Ipomoea cairica, J. Braz. Chem. Soc., Vol. 8, No. 3, 235-238,.

Pàska C., Innocenti G,.Kunvári M, M. László, L. Szilágyi, (1999) ,Lignan production by Ipomoea cairica callus cultures, Phytochemistry, 52, 879–883

Rastogi R. P., Mehrotra B. N., (2001) '*Compendium of Indian Medicinal Plants*', National institute of science communication, New Dehli, , Vol. 3, pg. 364.

Rong-Jyh Lin., Chung-Yi Chen.,. Wen-Li Lo, (2008) Cytotoxic Activity of Ipomoea cairicaNatural Product Research**,** 22(9), 747-753