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Short Report.

LIGNANS AND SESQUITERPENE LACTONES FROM THE ROOT BARK OF ARTEMISIA ARGENTEA

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ABSTRACT

The root bark of Artemisia Argentea L'Her (Asteraceae) contain besides the known sesquiterpene lactones, arborescin [1], argentiolide B [3], deacetyl argentiolide B[2] and artemolin [4] previously isolated from the aerial parts of the same plant, a group of lignan compounds namely (+)-sesamin [5], aschantin [6] and demethoxy excelsin [7] isolated from the plant for the first time.

All the known compounds were identified by spectroscopic analysis and comparison with authentic reference materials isolated from the aerial parts or by comparison with data cited in the literature.

INTRODUCTION

In connection with our interest on biologically active natural products[1,2], we investigated the chemical constituents of the root bark of Artemisia argentea L'Her. A large number of sesquiterpene lactones and tetrahydrofurofuran lignans were previously reported from over hundred Artemisia species[3-5]. Since this type of lignan compounds have been shown to possess some insecticidal[6] as well as medicinal properties[7,8], study of the chemistry of the title plant was deemed necessary to isolate its biologically active constituents.

EXPERIMENTAL

All mps were taken on an Electrothermal Melting Point Instrument in open capillaries and are uncorrected. MS were determined at 70 eV by direct insertion on a probe. ^{1}H-NMR spectra were obtained at 400 MHz using TMS as an int. Standard. IR spectra were run on a Unicam SP-1025 instrument in KBr discs. Column chromatography was carried out using silica gel (60-160 mesh) and TLC on Silica gel GF_{254} [E.Merck], two solvent systems were used C_6H_6-EtOAc (9:1 and 8:2), plates visualized by spraying with H_2SO_4 50% and subsequent heating at 100°C for 5-10 min.

Material :

The root bark was collected from plants cultivated in the Experimental Station of Medicinal Plants in Assiut University during April and May 1986.

Extraction and Isolation:

Dried and milled root bark (350 gm) was extracted with $CHCl_3$ (1 L) at room temp. for 24 hrs. The process was repeated twice and the $CHCl_3$ extracts joined and evaporated to give 18 g of dark brown thick oily residue, separated by column chromatography on 800 g Silica gel. Gradient elution was carried out with hexane with increasing proportions of EtOAc.

With EtOAc-hexane (2:23), 800 mg (arborescin), mp 144°C (Lit. 145°C)[6] and 430 mg (sesamine), mp 121°C (Lit. 120-121°C)[3]. EtOAc-hexane (1:9), 200 mg (+)-demethoxyexcelsin] mp 100°C (Lit. 101-102°C)[11] and 30 mg (argentiolide B). EtOAc-hexane (1.5:8.5), 80 mg (artemolin), mp 205°C (Lit. 205°C) and 30 mg (deacetyl argentiolide B), mp 183°C. EtOAc-hexane (2:8), 50 mg (aschantin) mp 68.5 (Lit. unreported).

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RESULTS AND DISCUSSION

The isolated sesquiterpene lactones have been identified through its pattern of isolation and R_f by TLC screening and by co-chromatography with authentic reference materials[1,2]. Its ^{1}H-NMR spectra confirm and amplify the conclusion. The isolated lactones were arborescin[9], argentiolide B[1] and its deacetyl derivative[1,2] and artemolin[2].

The ^{1}H-NMR spectra of other compounds (Table 2) indicated that it should be 2,6-diaryl-3,7-dioxabicyclo [3,3,0]-octane, i.e. lignans of the fused bistetrahydrofuran series, and the assignments of signals due to aromatic protons, methylenedioxy protons and methoxyl protons gave a confirmative informations about the pattern of substitution on the aromatic moieties. From the chemical shifts of the methine protons at C-1, C-5 (δ 3.06-3.18 m) and from the two sets of equivalent methylene protons, associated with C_4 & C_8 (δ 4.25-4.40 dd), it is clear that the isolated lignans fall under the symmetrical diequatorial series; this is because the two equatorial methylene protons are moved downfield due to the deshielding effect of the equatorial aryl groups[3].

A common character for the isolated lignans demonstrated by a positive Labat test[10] and significant fragment ions resulting from the dual breakdown at m/e 121,125 and 149 corresponds to the methylenedioxphenyl substituents.

Additional fragment ions at m/e 164, 161 due to "Sideways" and "Lengthwise" degradation of the bicyclo [3,3,0]-octane lignan-skeleton are evidenced[11,12].

Comparing the data of the obtained compounds (Table 1,2] with that cited in the literature[3], clearly demonstrated that

the compounds should be (+)-sesamin : 2,6-(diequatorial)-dipiperonyl-3,7-dioxabicyclo [3,3,0]-octane[13]; Aschantin: 2,6-(diequatorial)-2-trimethoxyphenyl, 6-piperonyl-3,7-dioxabicyclo [3,3,0]-octane[14] and (+)-demethoxyexcelsin: 2,6-(diequatorial)-2[3', 4'- methylene dioxy-5'- methoxyphenyl], 6 [3", 4" methylenedioxyphenyl]-3,7-dioxabicyclo-[3,3,0]-octane[14].

This is the first report on isolation of this type of lignan compounds from Artemisia argentea.

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Table 1: Characters of the Isolated Lignans

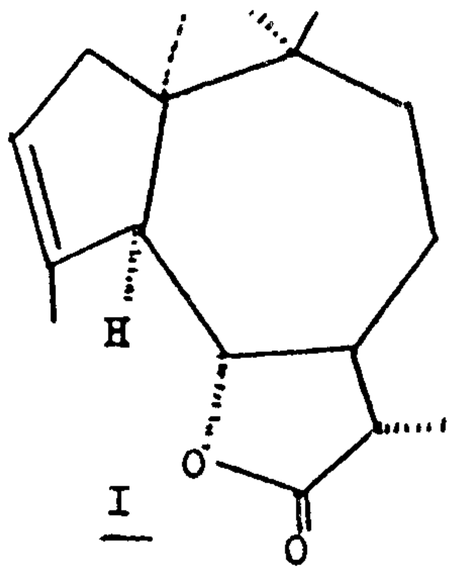
Compound	Formula	mp.	R*	IR	Yield %
(+)-Sesamin	$C_{20}H_{18}O_6$	121°C	0.88	2820,3020,1504, 1490,1445,1245, 880 ,830 ,810 cm^{-1}	0.530
Aschantin	$C_{22}H_{24}O_7$	68.5°C	0.75	2820,3020,1593, 1504,1490,1463, 1042,1011 cm^{-1}	0.033
(+)-Demethoxy-excelsin	$C_{21}H_{20}O_7$	100°C	0.58	2820,3020,1640, 1500,1440,1250, 1140,1095,940 , 830 ,815 cm^{-1}	0.133

R* Solvent: Benzene/EtOAc (8:2).

Table 2: ^{1}H-NMR Spectra of the Isolated Lignans

Proton	Sesamin	Aschantin	Dem.excelsin
1 H	3.06 m	3.10 m	3.18 m
2 H	4.73 d	4.76 d	4.72 d
4_α H	4.25 dd	4.30 dd	4.14-4.40 m
4_β H	3.88 dd	3.94 dd	3.75-3.97 m
5 H	3.06 m	3.10 m	3.18 m
6 H	4.73 d	4.76 d	4.72 d
8_a H	4.25 dd	4.30 dd	4.14-4.40 m
8_B H	3.88 dd	3.94 dd	3.75-3.97 m
OCH_3	-	3.91(2 Me) 3.87(1 Me)	3.92
O_2CH_2	5.95 s	5.98 s	5.94,5.95
Aromatic	6.86 m, 6.80 m,	6.86 m(3H) 6.58 s(2H)	6.9 m, 6.54 s

All values of δ relative to TMS in $CDCl_3$ at 400 MHz.



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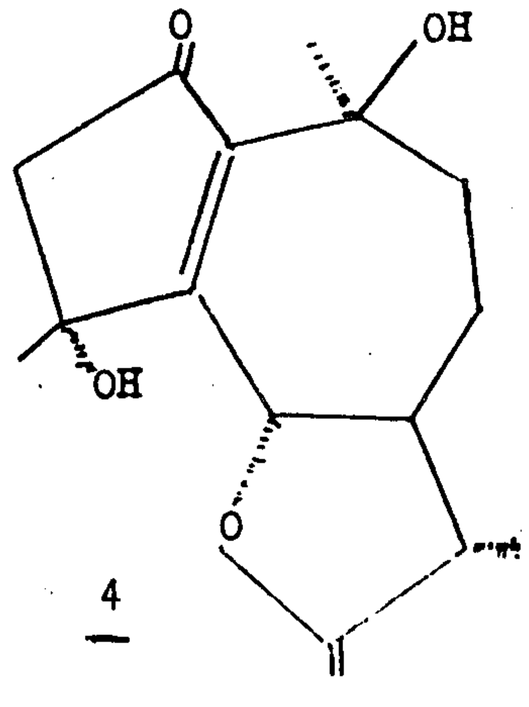

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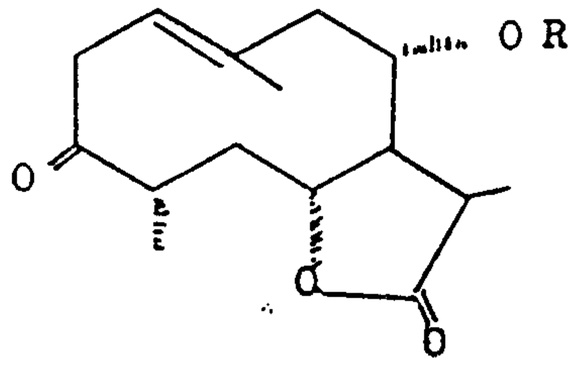
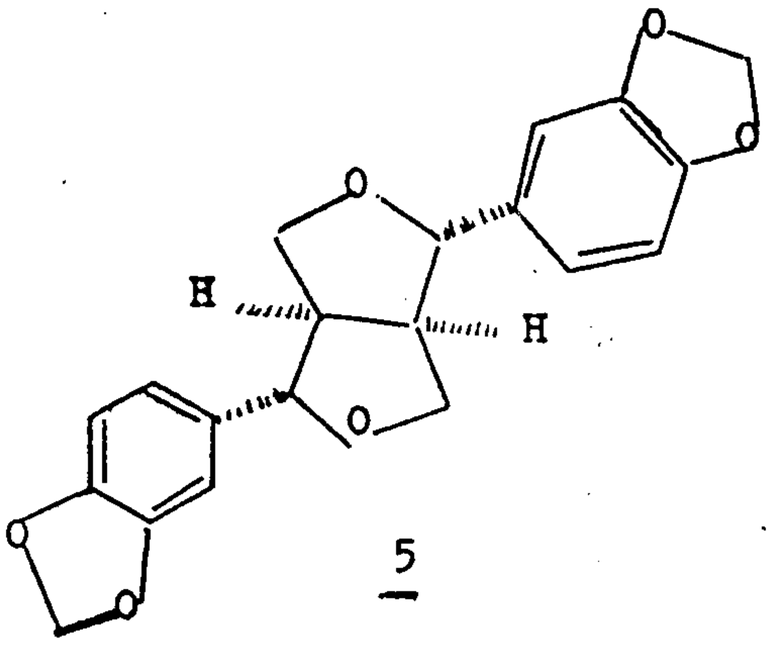


2 : R = AC

3 : R = H



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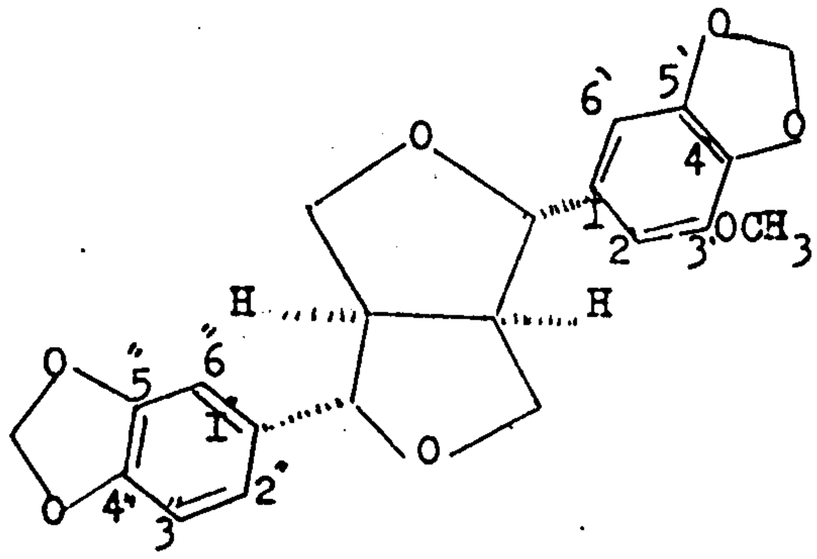

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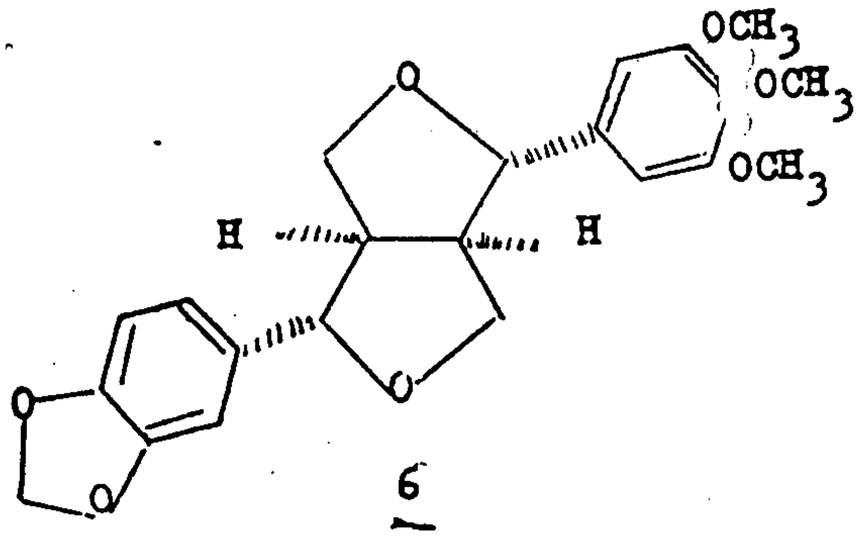

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ليجنانز وسسكيتربينات لاكتونية من قشور جذر الارتيميزيا ارجنتيا لير

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تم بدراسة خلاصـــة الكلورفورم لقشور الجذور فصل مجموعة مـــــــــن السسكيتربينات اللاكتونيه التى سبق فصلها من الأجزاء العلويـــــــة مـــــــن النبات وهذة اللاكتونـــات هى الاربوريســـــين ـ الارجنتيوليد ب ـ دى اسيتيـــل ارجنتيوليد ب والارتيمولين ٠

كذلك تم فصـــل مجموعه من الليجنانز لاول مرة من هـذا النبـــــات وهى السيسامـــين ، الاسكانينن وديميثوكســـى اكسلســـين ٠

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