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GALATICAT, A NEW DITERPENE FROM *SIDERITIS GALATICA*

SİDERÎTİS GALATICA 'DAN YENİ BİR **DİTERPEN:** GALATİCAT

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ÖZET

Sideritis galalica adlı bitkinin toprak üstü kısımlarından petrol eteri ekstraksiyonu ile yeni bir diterpen-lakton izole edildi, spektroskopik yöntemlerle (FT-IR, 1H NMR, ^{13}C NMR, APT, GC-MS) yapısı aydınlatılarak galaticat adı verildi.

ABSTRACT

Galaticat, a new lacton-diterpene, has been isolated from the petroleum ether extract of aerial parts of Sideritis galatica. Its structure has been identified by spectroscopy (FT-IR, ^{1}H NMR, ^{13}C NMR, APT, GC-MS).

Key Word: Sideritis galatica; galaticat; lacton-diterpene; ent-15,16,17,20- tetra-nor-5,9-dihidroksi-6,19-lacton labda-11-en

INTRODUCTION

Sideritis galatica is an endemic species growing in Kazan (Ankara, Turkey)(1). *Sideritis* species are used in Mediterranean traditional medicine for their antiinflammatory(2,3), antimicrobial activity(2). The genus *Sideritis* is reported to contain diterpens(4-8), terpenoids(9), sterols(4), flavonoids, coumarins, lignins, iridoids and phenolic constituents(2).

EXPERIMENTAL

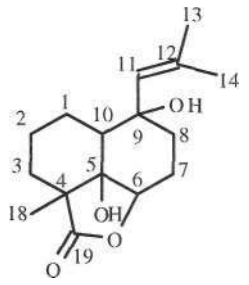
The melting point was determined in sealed capillaries and is uncorrected. FT-IR spectra were recorded on a Matson 1000 spectrometer. ^{1}H NMR and ^{13}C APT spectra were obtained with a Varian Gemini 200 (200 MHz) NMR spectrometer using $CDC1_3$ as a solvent unless otherwise indicated. All chemical shifts are reported ppm downfield from internal tetramethylsilane. Electron impact mass spectrometry at an ionization potential of 70 eV was performed with a Micro MASS UK Platform GC-MS.

Plant Material: *Sideritis galatica* was collected from Kazan region of Turkey in August 1996. The specimen is identified in Herbarium of the Biology Department, Gazi University.

Isolation of Diterpene: Dried and finely divided plants (1.60 kg *S. galatica),* were Soxhlet extracted with petroleum ether (b.p. 40-60 °C) in 72 hr. The petroleum ether extract was concentrated to 700 mL and then extracted (4x500 mL) with 90 % aqueous MeOH. The methanolic extract was collected and concentrated to 500 mL by rotary evaporator. Then, total volume was diluted with water to 2000 mL. This solution was extracted with chloroform (8x250 mL) and chloroform extracts were collected and evaporated until dryness(8). The oily residue was obtained in the flask.

The oily residue was dissolved in chloroform and purified by column chromatography (eluant $CHCl_3$:MeOH 9:1). The similar fractions were collected. Four different extracts were collected from the column. Because of the amounts were too small, three of them couldn't purified. The latter was purified by thin layer chromatography (development solution, $CHCl_3$:MeOH 9:1 ; stationary phase, silica gell 60 $PF_{254+366}$). The obtained product was crystallized from acetone (mp:66-67 °C).

RESULTS AND DISCUSSION



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Galaticat (1), mp 66-67 °C, $C_{16}H_{24}O_4$ (mass spectra, *m/z:* [M] 280). Its IR spectrum (Figure 1) showed characteristic absorptions for a carbonyl function at 1735 cm^{-1} , a carbon-carbon double bond at 1635 cm^{-1}, vinylic carbon-hydrogen bond stretching at 3043 cm^{-1}. The ^1H NMR spectrum of galaticat, **1**, (Figure 2) showed three methyl groups at approximately δ 0.9 ppm (s-broad, 9H); a vinylic proton (on C-l 1) at 7.35 ppm as singlet (it shifted to down field because of influence of C-OH group); proton on C-6 at 4.05 as triplet; also protons on C-7 at 1.6 ppm as multiplet, proton on C-10 2.29 at ppm as triplet. See also Table 1 for chemical shifts and peak

multiplicities of compound **I** .The ^{13}C APT spectrum of *1* (Figure 3) confirmed the proposed structure (see Table 2).

Table 1. Chemical shift data (δ, ppm) and peak multiplicities of protons of compound I

7.35 (s, 1H, on C-ll); 5.10 (s, 1H, on C-9 OH); 4.05 (t, 1H, on C-6); 2.29 (t, 1H, on C-10); 2.04 (broad, 1H, on C-5 OH); 1.6 (m, 4H, on C-7 and C-8); 1.2 (broad, 6H, on C-1, C-2 and C-3); 0.9 (broad :5, 9H, on C-13, C-14 and C-18)

Table 2. APT' Spectral data of compound 1 (in CDCI3)

C	APT	δ(ppm)	C	APT	δ(ppm)
1	CH_2	36.4	9	C	114.0
2	CH_2	24.6	10	CH	96.0
3	CH_2	34.2	11	CH	137.0
4	C	66.3	12	C	127.0
5	C	79.3	13	CH_3	16.1
6	CH	99.0	14	CH,	16.1
7	CH_2	31.3	18	CH_3	25.4
8	CH_2	33.9	19	C	175.9

For example , lacton carbonyl group at 175.9 ppm(APT - C); three methyl groups at 16.1 ppm, 16.1 ppm, 25.4 ppm (APT - CH_3) and carbon atoms bearing -OH group at 78 ppm apparent in APT spectrum. Also, molecular ion peak was observed at 280 *m/z* (M). All these results confirm the proposed structure.

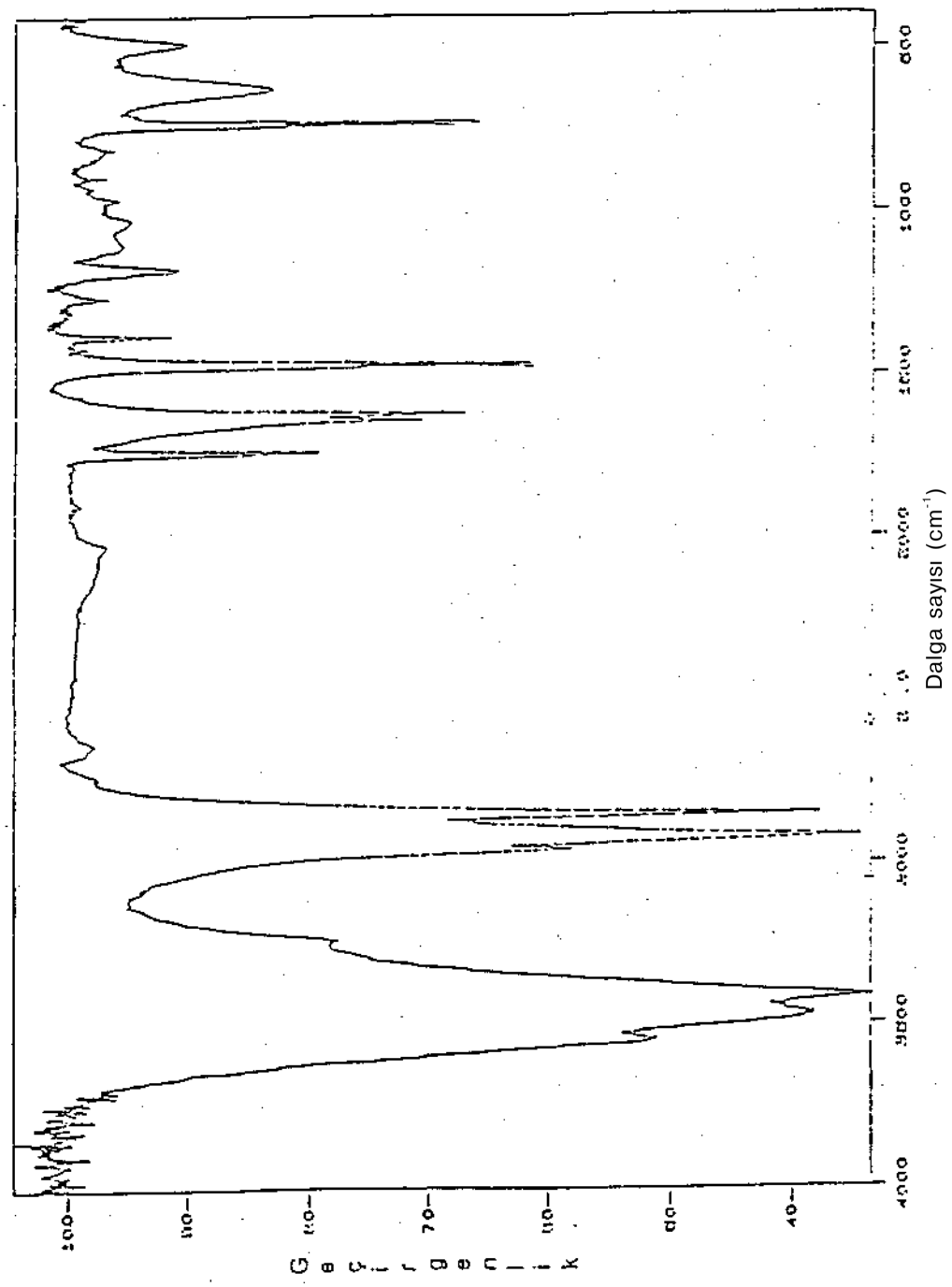

FIGURE 1: The IR spectrum of galaticat

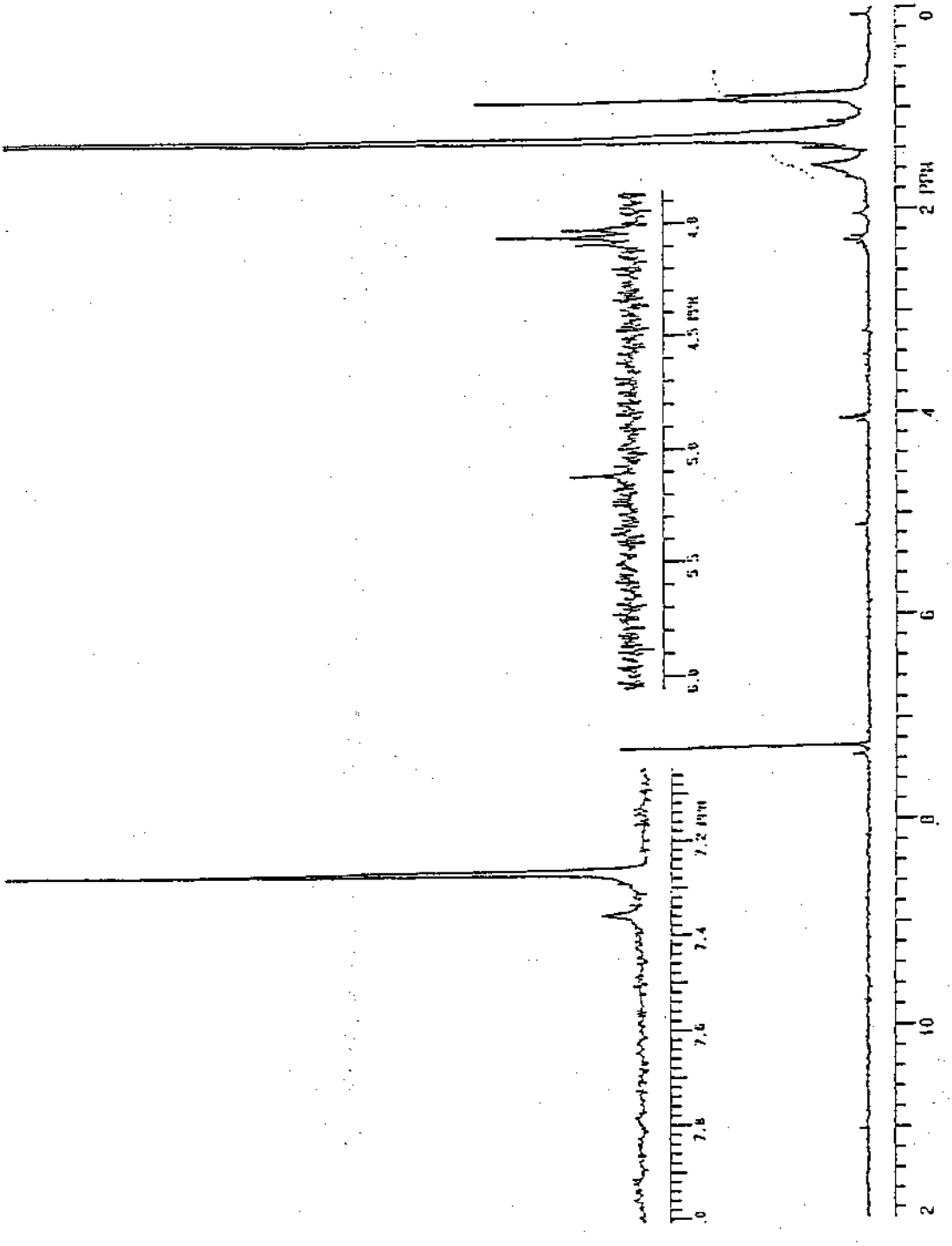

FIGURE 2: The ^{1}H NMR spectrum of galaticat

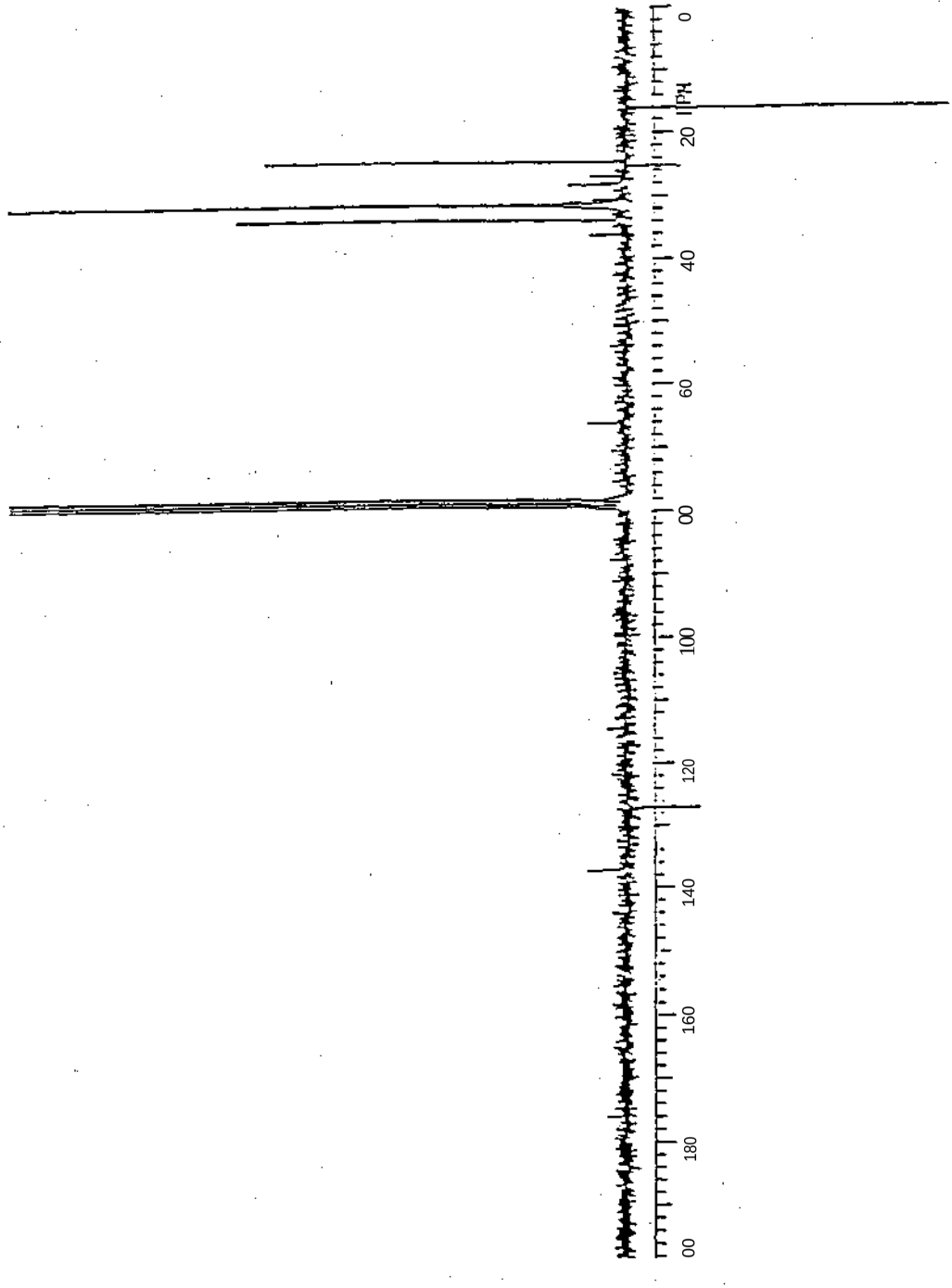

FIGURE 3: The APT spectrum of galaticat

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