

CAPILLARIN AND SCAPORONE FROM *ARTEMISIA LAMPROCAULOS*

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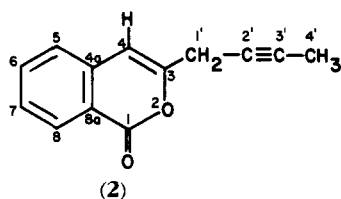
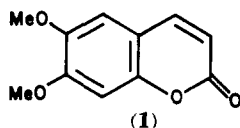
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In this first chemical investigation of *Artemisia lamprocaulos* Reehinger (Compositae), we report the isolation of scaporone (**1**) as well as the rare aromatic acetylenic compound capillarin (**2**), a substance previously isolated from *Chrysanthemum frutescens* L. and *Artemisia dracunculus* L. (1, 2) and later found in *Anthemis fuscata* Brot. (3). Because little spectral information was presented previously, we discuss here the ^1H -nmr data for capillarin and provide unreported ^{13}C -nmr data.

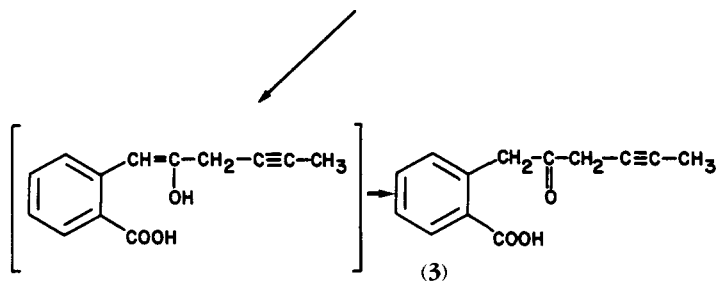
Spectra were recorded on the following instruments: ^1H -nmr in NT-200 MHz instrument; ^{13}C -nmr, Brücker WH-90; ms, DuPont-490; uv, Varian Techtron 635; and ir, Nicolet 7000 FT-IR.

PLANT MATERIAL.—*Artemisia lamprocaulos* was collected near Polur, 70 km east of Tehran, Iran, in September 1980, by Y. Aynehchi. A voucher specimen (No. 117) is deposited in the Herbarium of Faculty of Pharmacy, University of Tehran.

ISOLATION OF THE COMPOUNDS.—Air-dried, powdered leaf material (2.7 kg) was extracted with MeOH. Upon evaporation of the



+ 2 N HCl

EXPERIMENTAL¹

GENERAL EXPERIMENTAL PROCEDURES.—

¹Full details of the extraction and isolation of the compounds are available from the senior author on request.

MeOH, 240 g of residue were obtained. A 75-g aliquot was chromatographed over a silica gel column.

Scaporone (**1**).—Yield 700 mg, mp 145° [Lit. 144-146°; (4)]. ^1H -nmr (CDCl_3 , TMS): δ 3.90 (3H, s) and 3.94 (3H, s) for the OCH_3 groups; 7.65 (1H, d, $J=9$ Hz, H-4); 6.3 (1H, d, $J=9$

Hz, H-3); and 6.85 (2H, s, H-5 and H-8). Ms, m/z : M^+ , 206 (100%); M-15, 191 (50%); M-28, 178 (18%).

Capillarín (2).—Yield 237 mg, mp 120°, uv (MeOH) 322, 268, 259, 250 (sh), 237, 227, 200 nm [Lit. (2) recorded in ether: 321, 275, 264, 255, 239, 227 nm]. Ir (in KBr) 2950, 1725, 1680, 1600, 1570, 1480, 1360, 1320, 1170, 1050, 1020, 750, and 680 cm^{-1} . Although very low intensity bands for the acetylenic function were previously reported (2), even with Fourier transform ir, no absorption could be observed in the 2250 cm^{-1} region of the spectrum in accord with the almost symmetrical nature of the triple bond. ^1H -nmr (in CDCl_3 , TMS): δ 1.82 (3H, t, $J=3$ Hz, 4'- CH_3); 3.38 (2H, m, 1'- CH_2); 6.55 (1H, d, $J=1$ Hz, H-4); 8.18 (1H, brd, $J=8$ Hz, H-8); 7.62 (1H, dt, $J=8$ Hz and 2 Hz, H-6); 7.40 (1H, brt, $J=8$ Hz, H-7); and 7.34 (1H, brd, $J=8$ Hz, H-5). The assignments for the aromatic proton signals were based on spin-decoupling experiments in CDCl_3 as well as benzene- d_6 ; in the latter solvent, slightly better resolution of the signals was achieved. The relationship between the methyl and methylene group was also established by spin-decoupling experiments. When the methylene signal at δ 3.38 was irradiated, the methyl triplet ($J=3$ Hz) collapsed to a sharp singlet. This is a typical interaction between a methyl and methylene over one acetylenic bond (5). The same irradiation also caused the H-4 doublet ($J=1$ Hz) at δ 6.55 to collapse to a singlet. Reciprocal irradiation of the signal at δ 6.55 simplified the methylene multiplet to a quartet ($J=3$ Hz). ^{13}C -nmr (CDCl_3 , TMS): 162.6 (s) lactone carbonyl; 153.9 (s) C_3 ; 137.4 (s) C_{8a} ; 134.9 (d) C_8 ; 129.7 (d) C_7 ; 128.05 (d) C_6 ; 125.5 (d) C_5 ; 120.2 (s) C_{4a} ; 103.2 (d) C_4 ; 79.9 (s)

C_3 ; 71.8 (s) C_2 ; 23.8 (t) C_1 ; 3.67 (q) C_4 . Ms, M^+ , m/z 198 (100%); M-15, 183 (2%); M-28, 170 (10%); M-29, 169 (10%); M- C_4H_5 , 145 (40%); C_4H_5^+ , 89 (84%); C_4H_5^+ , 63 (24%).

ACID TREATMENT OF CAPILLARIN.—The ring opening of capillarín was performed with 2 N HCl in order to distinguish its isocoumarin skeleton from that of a coumarin. The reaction afforded the expected keto-acid (3). The ir of 3 showed a small OH peak at 3420 cm^{-1} and bands for two carbonyl groups at 1725 and 1705 cm^{-1} for the free acid and the ketone group. The nmr showed an extra CH_2 group at δ 3.65 ppm, while the original CH_2 quartet shifted to δ 2.6 ppm; ms gave an M^+ peak at m/z 216.

ACKNOWLEDGMENTS

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