THE VOLATILE CONSTITUENTS OF THE ROOTS OF *SELINUM TENUIFOLIUM*

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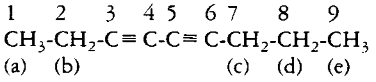
The occurrence of trace amounts of polyacetylenes has been reported in Umbelliferae (1). The volatile oil of *Selinum tenuifolium* Wall. (Umbelliferae) has been reported to possess antibacterial property (2). Sood *et al.* (3) reported limonene, elemol, terpineol, geraniol, and eudesmol as the major constituents of the essential oil of *S. tenuifolium*. In contrast to the results reported by Sood *et al.*, we have observed distinct peaks at 2180 cm^{-1} and 2280 cm^{-1} in the ir spectrum of the oil, indicating the presence of acetylenic structure. Gas chromatographic analysis revealed the major component to be as much as 91 ± 1% of the total oil. This acetylenic compound was also observed in similar proportions in the oil obtained by cold (~20°) extraction of roots with petroleum ether, thus eliminating the possibility of it having been formed during steam distillation. This component was separated by preparative gc. Its structure, 3,5-nonadiyne (**1**), was deduced from spectroscopic data (Table 1) and further supported by its synthesis. The unequivocal assignment of cmr chemical shifts of (**1**), for example, C-3 vs. C-6 and C-4 vs. C-5, were made by using 3,5-nonadiyne-1,2-^{13}C. This compound was prepared from 1,3-heptadiyne and ethyl iodide -1,2-^{13}C (single-labeled ethyl iodide-1-^{13}C would have been preferable for our study, but only the double-labeled compound was available). The gc/ms of the oil also indicated the presence of small amounts (<1% each) of α-pinene, 5-nonen-3-yne, and 1-nonen-3,5-diyne. This communication constitutes the first report of the occurrence of 3,5-nonadiyne in a plant.



$$\underset{(a)}{\overset{1}{CH_3}}\text{-}\underset{(b)}{\overset{2}{CH_2}}\text{-}\overset{3}{C}\equiv\overset{4}{C}\text{-}\overset{5}{C}\equiv\overset{6}{C}\text{-}\underset{(c)}{\overset{7}{CH_2}}\text{-}\underset{(d)}{\overset{8}{CH_2}}\text{-}\underset{(e)}{\overset{9}{CH_3}}$$

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TABLE 1. Cmr, Pmr, Ir, and Ms Data of 3,5-Nonadiyne (**1**)

Cmr Chemical Shifts[a]		Pmr Chemical Shifts[a]		Infrared (cm^{-1})	Ms *m/z* (rel. int.)
C-1	13.6	CH_3 (a)	1.16	2180	120[M]$^+$ (100)
C-2	13.0	CH_2 (b)	2.25	2280	105[M-CH_3]$^+$ (54)
C-3	77.7				
C-4	65.5	CH_2 (c)	2.22		91[M-C_2H_5]$^+$ (79)
C-5	66.2	CH_2 (d)	1.54		77[M-C_3H_7]$^+$ (60)
C-6	76.5				
C-7	21.3	CH_3 (e)	0.98		
C-8	22.2				
C-9	13.5				

[a] The cmr and pmr spectra were recorded on a Varian XL-100-15 spectrometer and JEOL FX-90 spectrometer. All samples were run neat with internal TMS in 5 mm tubes which were inserted coaxially in 12 mm tubes containing D_2O for field frequency locking. Chemical shifts are given in ppm downfield from TMS.

EXPERIMENTAL

PLANT MATERIAL.—The roots of *S. tenuifolium* were collected from the Cheena peak area in Nainital, India. The identity of the plant was confirmed by Professor Y.S. Pangtey of the Botany Department, Kumaun University, Nainital.

ISOLATION OF 3,5-NONADIYNE.—The fresh roots (2 kg) were shredded and steam distilled. The aqueous distillate was extracted with petroleum ether (60-80°). The extract worked up in the usual way gave 2.4 g (0.12%) of pale yellow oil. 3,5-Nonadiyne was separated from the oil by preparative gc.

Another 1.25 kg of root material was extracted with cold (~20°) petroleum ether (40-60°). Work-up of the extract gave 2.2 g (0.17%) of orange-red oil. The gc analysis of this oil showed it to contain >84% of 3,5-nonadiyne.

SYNTHESIS OF 3,5-NONADIYNE.—A slurry of $NaNH_2$ in liquid NH_3 was prepared from 0.25 g (0.011 mole) sodium. To the slurry were added dropwise, 0.92 g of 1,3-heptadiyne (4) in 2 ml DMSO and then 1.872 g (0.012 mole) C_2H_5I in 2 ml DMSO. The reaction mixture was stirred for another 30 min and the NH_3 allowed to evaporate. Et_2O (50 ml) was added to the residue, followed by 20 ml of H_2O (dropwise). The aqueous layer was extracted with two 25-ml portions of Et_2O; these were combined with the original Et_2O layer and dried over anhydrous $MgSO_4$. After filtration, evaporation of the Et_2O under reduced pressure left an oil that upon short-path distillation gave 1.05 g (88%) of 3,5-nonadiyne, bp 75-78°/15 mm. A portion of the distillate purified further by preparative gc exhibited spectra (Table 1) identical to those of the 3,5-nonadiyne isolated from the oil.

3,5-Nonadiyne-1,2-^{13}C was prepared analogously from 1,3-heptadiyne and ethyl iodide-1,2-^{13}C (90% ^{13}C at CH_2 and 63% ^{13}C at CH_3).

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CONSTITUENTS OF THE ESSENTIAL OIL OF *BLEPHAROCALYX TWEEDIEI*

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In continuation of our research (1) on essential oils from Argentine indigenous plants, we now report the composition of an essential oil from *Blepharocalyx tweediei* Berg (Myrtaceae) with an anomalously high content of verbenone and carvone, as far as we know only surpassed by *Eugenia pseudomato* essential oil (2). The pleasing odor of this essential oil and high content of myrtenal and verbenone make it a potential new natural source of those chemicals, possibly useful in perfumery.

This tree is a medicinal plant commonly used against pulmonary and throat disease (3-4) with antispasmodic, antiseptic, and balsamic properties. Two different samples were investigated, one of green leaves and the other, a commercially dried and milled plant material. The latter provided less yield of essential oil than did fresh material, with the absence of α-thujene, α-terpinol, and citronellol.

As far as we know, this is the first full report on an essential oil from the genus *Blepharocalyx* (5).