

Table 1. NMR spectral data for 1,8,11,14-heptadecatetraene

δ	No. of protons	Type	J (Hz)	Interpretation
0.98	3	<i>t</i>	8	CH_3-CH_2-
1.36	6	<i>bs</i>		$-\text{CH}_2-(\text{CH}_2)_3-\text{CH}_2-$
2.05	6	<i>m</i>		$-\text{CH}_2-\text{CH}_2-\text{CH}=$
2.81	4	<i>t</i>	5	$=\text{CH}-\text{CH}_2-\text{CH}=$
4.94	1	<i>d,m</i>	10	$-\text{CH}_2-\text{H}-(-\text{C}=\text{C}-)\text{H}-\text{H}$
4.98	1	<i>d,m</i>	17	$-\text{CH}_2-\text{H}-(-\text{C}=\text{C}-)\text{H}-\text{H}$
5.37	6	<i>m</i>		Nonconjugated vinyl H
5.84		<i>d,d,t</i>	17,10,6	$-\text{CH}_2-\text{CH}=\text{CH}_2$

these compounds was effected on a Si gel H column with hexane-Et₂O.

GLC on a Silar 5CP column indicated that one component constituted 96% of one fraction. An exact mass measurement with a DuPont (CEC) 21-110A high resolution mass spectrometer gave C₁₇H₂₈ as the molecular formula. MS: M⁺ *m/e* 232 (4%), 108 (80), 95 (48), 93 (48), 91 (29), 81 (39), 80 (56), 79 (100), 67 (65), 55 (36), 41 (37). The 100 MHz NMR spectrum was taken in CDCl₃ with TMS as internal standard. Analysis of the spectrum (Table 1), aided by double resonance decoupling experiments, established the identity of the hydrocarbon as 1,8,11,14-heptadecatetraene.

The IR spectrum of the heptadecatetraene (neat) accords with that described by Romaňuk *et al.* [2], showing peaks at 3012, 1641, 992 and 911 cm⁻¹. No peak at 974 cm⁻¹ showing *trans* unsaturation is present, so the disubstituted double bonds have the *cis* configuration. The UV spectrum of a sample purified by GLC shows a

continually increasing absorption from 220 nm to the instrument cutoff point at 182 nm (ϵ 38400) (cyclohexane) with an inflection at 193 nm (ϵ 26300). (The recorded spectrum of an equimolar mixture of methyl linolenate and methyl 10-undecenoate is very similar in shape and intensity).

The amount of heptadecatetraene in a hexane-acetone extract of 4-day-old seedlings grown from 1000 g seed was 0.28 g. An estimate of the amount of heptadecatetraene in a hexane-acetone extract of 4-day-old seedlings showed 0.028%.

Carthamus tinctorius and *Saussurea lappa*, the only plants in which the presence of 1,8,11,14-heptadecatetraene is reported, are both members of the tribe Cynareae.

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ECHINATINE AND SUPININE: PYRROLIZIDINE ALKALOIDS FROM *EUPATORIUM CANNABINUM*

ERLING PEDERSEN

Chemical Laboratory B, The Royal Danish School of Pharmacy, Universitetsparken 2, DK 2100 Copenhagen Ø, Denmark

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Plant. *Eupatorium cannabinum* L.—Compositae. **Source.** Vaserne, north of Copenhagen. Voucher specimen in the herbarium of the Botanical Museum, University of Copenhagen. **Uses.** Eme-

tic and diuretic [1]. **Previous work.** Sesquiterpene lactones [2, 3], flavonoids [4], sterols [5].

Present work. The MeOH extract of the dried aerial parts (2 kg) was evaporated and the residue

extracted with 1 N H_2SO_4 . The filtrate was made alkaline with conc NH_4OH and extracted with CHCl_3 . The CHCl_3 solution was dried with MgSO_4 and evaporated to give crude alkaloid (0.6 g), containing echinatine and supinine in roughly equal parts.

In order to obtain alkaloids present as N -oxides, the alkaline soln was acidified with 4 N H_2SO_4 to pH 3, reduced with Zn dust over night, filtered and made alkaline and re-extracted with CHCl_3 . Evaporation of dried CHCl_3 extract gave crude alkaloid (1.2 g), containing mainly echinatine. Pure alkaloids were obtained by chromatography on Si gel with $\text{CHCl}_3\text{-MeOH}$ mixtures followed by rechromatography on microcrystalline cellulose with $n\text{-BuOH-HOAc-H}_2\text{O}$ (80:3:17). Column effluents and homogeneity of the alkaloids were controlled by paper and TLC chromatography [6].

Echinatine [7, 8] was isolated as a gum, $[\alpha]_D^{22} +12^\circ$ (c 2.0, EtOH), which could not be crystallized, but formed a picrolonate mp 205–7° (decomp.). Alkaline hydrolysis gave heliotridine mp 115–6° and (–)-viridifloric acid mp 127–9°, $[\alpha]_D^{22} -1.0^\circ$ (c 2.0, H_2O), brucine salt mp 193–5°. The alkaloid and its derivatives was identical with

echinatine isolated from *Cynoglossum officinale* L. by mmp, IR and MS data. Supinine [8, 9] was isolated as colorless needles, mp 143–4°, $[\alpha]_D^{22} -12^\circ$ (c 1.0, EtOH). Alkaline hydrolysis gave supinidine with picrate mp 141–2° and (+)-trachelanthic acid mp 90–1°, $[\alpha]_D^{22} +2.0^\circ$ (c 2.0, H_2O). This alkaloid was shown to be supinine from IR and MS data.

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CONSTITUENTS OF COTTON BUD ESSENTIAL OIL

P. A. HEDIN, A. C. THOMPSON and R. C. GUELDNER

Boll Weevil Research Laboratory, Agric. Res. Serv., USDA, Mississippi State, MS 39762, U.S.A.

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Since 1965, a series of reports have been published from this laboratory concerning the constituents in the essential oil of the cotton bud (*Gossypium hirsutum* L. var Deltapine Smoothleaf) [1]. By GLC-MS of Si gel column fractions, 16 additional constituents have been identified (Table 1). These and the 59 previously identified constituents account for at least 57.3% of the total oil. The cumulative list of 75 includes 12 monoter-

pene hydrocarbons, 9 sesquiterpene hydrocarbons, 15 aliphatic carbonyl compounds, 4 aromatic carbonyl compounds, 30 alcohols and phenols, 4 other oxygen-containing compounds, and indole. The major constituents yet to be identified appear to be sesquiterpene alcohols, carbonyl compounds and oxides of M^+ 218, 220, and 222.