

ISOLATION AND ^{13}C NMR OF POLYACETYLENES
FROM *BACCHARIS ELEAGNOIDES*

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ABSTRACT.—From *Baccharis eleagnoides*, baccharis oxide and four polyacetylenes were isolated. This is the first time that (1,7*E*,9*Z*,15*E*)-heptadecatetraene-11,13-diyne is mentioned in the literature. The ^{13}C nmr of the natural polyacetylenes is reported.

Motivated by the limited information on the constituents of *Baccharis* (Compositae) that grow in our area, we began a survey of the chemical composition of arboraceous species from Sao Paulo and Minas Gerais, Brazil. Thus, *Baccharis eleagnoides* Stend (1) was studied, and from the crude extracts of the aerial parts and roots we have isolated baccharis oxide [1] (2), methyl-10-[(*Z*)-2-methyl-2-butenoyloxy]-(2*Z*,8*Z*)-2,8-decadiene-4,6-diynoate [2] (3), methyl-(8*S*)-8-[(*Z*)-2-methyl-2-butenoyloxy]-(2*Z*)-2-decene-4,6-diynoate [3] (4), and (1,7*E*,9*E*,15*E*)-heptadecatetraene-11,13-diyne [4] (5), which are known compounds. Their structures were established by comparison of their spectroscopic data with those reported in the literature.

(1,7*E*,9*Z*,15*E*)-Heptadecatetraene-11,13-diyne [5] is a new polyacetylene that was isolated from the leaves; its purification was hindered by its resemblance to 4 in its spectroscopic data and chromatographic behavior. Its structure was established from the following evidence. The uv spectrum showed typical absorption bands for an ene-diyne-diene chromophore (336, 314, 292, 267, and 252 nm), and the ir spectrum reveals the presence of a terminal vinyl group (915, 985, 1630 cm^{-1}) and acetylenic bonds [2200 (stronger) and 2120 cm^{-1}], characteristic of some *trans*-yne-ene isomers. The ^1H nmr of 4 supports this assignment. A double doublet at δ 1.80 ($J = 7.0$ and 1.5 Hz) is attributable to an Me-CH=CH grouping. A multiplet corresponding to four protons at δ 2.10 is most likely due to two methylene

groups close to double bonds. A multiplet at δ 1.40 can be ascribed to two normal methylene groups. The olefinic region (δ 6.90–4.80) is very complex and can be interpreted only incompletely. There is a multiplet at δ 4.94 and 4.92 showing typical splitting of a terminal vinyl group. The ^1H -nmr spectra of 4 and 5 are superimposable, showing minor differences in the complex olefinic region (δ 6.80–5.40). The ms spectrum exhibits a molecular ion at m/z [M] $^+$ 224 ($\text{C}_{17}\text{H}_{20}$) and a fragmentation pattern in agreement with the suggestion that 5 and 4 are stereoisomers. The ^{13}C -nmr spectra of 5 and 4 (Figure 1) indicated that the main differences between these two compounds were situated in the diene moiety and that a careful assignment of all carbons could solve this structure. Carbons 1 to 6 were assigned taking open-chain alkenes and dienes as model compounds (6). It was additionally observed that this moiety showed similar behavior in 4 and 5. Carbons 14 to 17 of 5 and 4 showed similar chemical shifts, their assignment involved the comparison between them and (*E*)-1-pentyne-3-ene and (*Z*)-1-pentyne-3-ene (6) taken as model compounds. The *Z* configuration at C-15 of both 4 and 5 was deduced from the chemical shift of Me-17 (18.6 ppm). The sp carbons showed different relaxation times and long range couplings. These observations led us to assign to C-12 and C-13 of 5 the two singlets resonating at 76.8 and 73.0 ppm due to their simpler fine structure and longer relaxation time than those singlets absorbing at lower field

ricaria ester derivatives (9) were taken as model compounds.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Mp's are uncorrected and were determined on a Reichert hot stage microscope. Ir spectra were recorded on a Perkin-Elmer 1430 spectrometer. Optical rotations were measured in a Carl Zeiss-Jena photoelectric polarimeter. ^1H -nmr spectra were recorded on a Bruker AW 80 (80 MHz) or on a Varian XL100 (100 MHz). ^{13}C -nmr spectra were recorded at 25.2 MHz on a Varian XL100 with CCl_4 (δ 96.0) as solvent and internal standards. Ms spectra were recorded on a Varian MAT 311 instrument.

PLANT MATERIAL.—*B. eleagnoides* roots (1.7 kg) and leaves (3.0 kg) were collected in Jundiá, São Paulo, Brazil, in May 1986, and identified by Prof. H.F. Leitão Filho. Voucher specimens are deposited at the Departamento de Botânica, Instituto de Biologia, Universidade Estadual de Campinas (2/IV/87 - UEC 46,664).

EXTRACTION AND ISOLATION.—Fresh leaves were milled and thoroughly extracted with cold Et_2O , yielding a crude extract (155 g), which was chromatographed on a Si gel column (800 g) using hexane and increasing amounts of Et_2O as eluent. The 80 fractions (500 ml) were further purified either by smaller silica column or preparative tlc on Merck PF₂₅₄ Si gel. The fractions were never totally evaporated and were kept in the refrigerator before taking the uv spectra, and those revealing the presence of polyacetylenes were handled with care and kept in dilute solutions at 5° to prevent polymerization. Evaporation of the solvent was done just before taking the spectra.

Fresh roots were milled and extracted with cold Et_2O , yielding 30 g of crude extract which was chromatographed on a Si gel column (300 g) using hexane and increasing amounts of Et_2O as eluent. The 35 fractions (200 ml) were monitored by uv, and those containing polyacetylenes were handled with care and further purified, by cc or preparative tlc. The remaining fractions were also submitted to further purification either by cc or tlc.

IDENTIFICATION OF THE ISOLATED COMPOUNDS.—The data of the known compounds corresponded to those published in the literature, and thus except for ^{13}C nmr they are not repeated. (+)-Baccharis oxide [1] (850 mg) was eluted with hexane from the root crude extract: mp, ir, nmr and ms were identical with those of Anthonsen *et al.* (2).

Methyl-10-[(Z)-2-methyl-2-butenyloxy]-

(2Z,8Z)-2,8-decadiene-4,6-dienoate **2** (350 mg), eluted with hexane- Et_2O (7:3) from the crude extract of the leaves and further purified by Si gel preparative tlc using hexane- Et_2O (8:2) as a solvent: uv, ir, ms, and nmr data identical with those of Bohlmann *et al.* (3). Methyl-(8S)-8-[(Z)-2-methyl-2-butenyloxy]-(2Z)-2-decene-4,6-dienoate [3] (120 mg) eluted with hexane- Et_2O (7:3) from the crude extract of the roots and further purified by Si gel cc using hexane and increasing amounts of Et_2O as solvent: uv, nmr, ms, and optical rotation and nmr of the 8-hydroxy derivative data identical with those of Bohlmann *et al.* (4).

(1,7E,9E,15E)-heptadecatetraene-11,13-diyne [4] (180 mg), eluted with hexane from the crude extract of the leaves and further purified by continuously eluting a Si preparative tlc with hexane: uv, ir, nmr, and ms data identical with those reported by Clin *et al.* (5).

(1,7E,9Z,15E)-heptadecatetraene-11,13-diyne [5] (80 mg) eluted with hexane from the crude extract of the leaves and further purified by continuously eluting a Si gel preparative tlc: uv λ (hexane) max (ϵ) 336 (26,000), 314 (34,000), 292 (28,000), 267 (25,100), 252 (29,000) nm; ir (CCl_4) ν max 2850, 2880, 2200, and 2120 ($\text{C}-\text{C}$), 1630, 985, 915 (terminal vinyl group) cm^{-1} ; ^1H nmr (80 MHz, CDCl_3) δ 6.70 (m, 1H, H-9), 6.20 (m, 1H, H-15), 5.70 (m, 1H, H-2), 5.45 (m, 2H, H-10, H-15), 4.94 (dm, 1H, H-1', $J = 11$ Hz), 4.92 (dm, 1H, H-1, $J = 16$ Hz), 2.10 (td, 4H, H-3, H-6), 1.80 (dd, 3H, H-17, $J = 7$ and 1.5 Hz), 1.40 (m, 4H); ms m/z [$\text{M}]^+$ 224 (38) ($\text{C}_{17}\text{H}_{20}$), 155 (45), 141 (100), 115 (56), 89 (20); ^{13}C nmr see Figure 1.

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