

POLYACETYLENES OF *SENECIO JACOBAEA*

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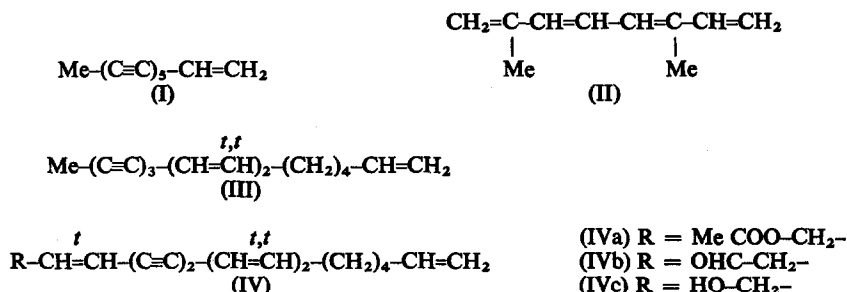
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Key Word Index—*Senecio jacobaea*; Compositae; acetylenes.

INTRODUCTION

THE GENUS *Senecio* has been widely investigated for its alkaloid content.¹⁻⁴ We wish to report the characterization of several acetylenic compounds from the common ragwort, *Senecio jacobaea* L. Previously, the pentayne-ene (I) has been isolated from the roots of various *Arnica* species and from the roots and flowers of *A. montana* L.⁵ Two C₁₁-polyacetylenes have been reported to be present in *Psilothonna tagetes*.⁶



RESULTS AND DISCUSSION

The crude extracts from the roots, leaves and flowers were first examined for the presence of polyacetylenes by UV spectroscopy. Only the extract from the flowers showed the presence of minute amounts of polyacetylenes.

The crude flower extract was chromatographed on a silica gel column and further purified by repeated column chromatography and/or preparative TLC. The first compound eluted from the column with light petrol. was the polyene hydrocarbon cosmene (II), easily recognizable by its characteristic UV spectrum.⁷ This compound was assayed spectrophotometrically, but otherwise not studied further, apart from co-chromatography with an authentic sample to prove identity.

A second hydrocarbon was eluted from the column by 10% Et₂O in light petrol. This compound possessed a diene-triyn chromophore (λ_{max} 348, 326, 307, 288, 268, 255 and

¹ R. B. BRADBURY and S. MOSBAUER, *Chem. & Ind.* 1236 (1958).

² R. B. BRADBURY, *Austral. J. Chem.* 9, 521 (1956).

³ T. A. GEISSMANN, *Austral. J. Chem.* 12, 247 (1959).

⁴ C. G. GORDON-GRAY and F. D. SCHLOSSER, *J. S. Afr. Chem. Inst.* 22, 165 (1969).

⁵ K. E. SCHULTE, J. REISCH and G. RUECKER, *Arch. Pharm.* 296, 273 (1963).

⁶ F. BOHLMANN and C. ZDERO, *Chem. Ber.* 104, 954 (1971).

⁷ P. NAYLOR and M. C. WHITING, *J. Chem. Soc.* 4007 (1954).

247 nm). The IR spectrum showed the presence of acetylene groups (2220 cm^{-1}), a *trans*, *trans*-olefinic group (990 cm^{-1}) and a vinyl group ($1320, 905\text{ cm}^{-1}$). After repeated purification by TLC the MS showed a molecular ion at m/e 222, corresponding to a molecular formula of $\text{C}_{17}\text{H}_{18}$. Structure (III) is in agreement with the MS fragmentation. This compound has previously been identified in other members of the Compositae.⁸

Two further compounds were eluted from the column by 10% Et_2O in light petrol. One possessed an ene-diyne chromophore (λ_{max} 284, 267, 253 and 241 nm), but was present in too small amounts to be fully characterized. However, the IR indicated an ester (1740 cm^{-1}) and, on hydrolysis, the product was much more polar than the starting material, this indicating successful hydrolysis. Treatment of the product with MnO_2 in Et_2O gave a remarkable shift in the chromophore, the hydrolysed and oxidized product possessing an ene-diyne-ene chromophore (λ_{max} 313, 294, 277, 265 and 249 nm). The structure of this product is still uncertain.

The second compound possessed an ene-diyne-diene chromophore (λ_{max} 337, 314, 296, 268 and 253 nm). The IR showed the presence of acetylenic groups ($2210, 2120\text{ cm}^{-1}$), an ester carbonyl (1735 cm^{-1}), carbon-carbon double bonds (1635 cm^{-1}), *trans*, *trans*-double bonds (990 cm^{-1}), *trans* double bond (950 cm^{-1}) and a vinyl group ($1415, 905\text{ cm}^{-1}$). The NMR spectrum of the compound showed the presence of 6 olefinic protons ($m, 3.2\text{--}4.8\tau$), 3 vinyl protons ($m, 5.1\tau$), an isolated methylene group ($dd, 5.5\tau, J$ 6 and 1.5 Hz), a single methyl group ($s, 8.0\tau$), 4 methylene protons adjacent to double bonds ($m, 7.9\tau$) and a further 4 methylene protons ($m, 8.6\tau$). The MS showed a molecular ion at m/e 282, corresponding to a molecular formula of $\text{C}_{19}\text{H}_{22}\text{O}_2$. Upon hydrolysis the IR peak at 1735 cm^{-1} disappeared and was replaced by a new peak at 3350 cm^{-1} , thus indicating a hydroxyl group. The MS showed a new molecular ion at m/e 240, indicating that the original ester was an acetate. On treatment of the hydrolysed product with MnO_2 the UV maxima shifted to 358, 345, 318 and 285 nm (Et_2O), indicating that oxidation had occurred. In MeOH the UV maxima become 340, 316, 297, 268 and 255 nm, indicating that the oxidized product is an aldehyde which has formed an acetal with methanol. The MS shows a molecular ion at m/e 238. These facts lead to the compound having structure (IVa), the aldehyde produced on oxidation thus being Vb.

Two further compounds were eluted from the column by 20 and 25% Et_2O in light petrol. UV spectra indicated that the two compounds were a diene-triyne and an ene-diyne, respectively. (λ_{max} 346, 324, 305, 283, 267 and 258 nm and 283, 266, 253 and 240 nm.) However, insufficient material was present to enable full characterization to be performed.

30% Et_2O in light petrol. eluted a compound (IVe) with an ene-diyne-diene chromophore. (λ_{max} 337, 316, 298, 283, 268 and 253 nm). IR spectra showed the presence of an alcohol group (3350 cm^{-1}), acetylenic groups ($2190, 2120\text{ cm}^{-1}$), olefinic groups (1640 cm^{-1}), a vinyl group ($1415, 905\text{ cm}^{-1}$) and *trans*, *trans*-double bonds (990 cm^{-1}). The NMR spectrum was identical to that of (IVa), except that the double doublet of IV, centred at 5.5τ was moved to 5.85τ , and there was no singlet methyl group at 8.0τ . Instead, the compound had a broad peak centred at 7.2τ , corresponding to 1 proton, which disappeared on treatment with D_2O . Oxidation of VI with MnO_2 gave a compound identical with the oxidation product obtained after hydrolysis of IVa, and IVc was found to be identical with the hydrolysis product of IVa. The results are in agreement with those previously published for the naturally occurring alcohol.⁹ The acetate (IVa) has previously been synthesized.¹⁰

⁸ F. BOHLMANN, E. INHOFFEN and P. HERBST, *Chem. Ber.* **90**, 124 (1957).

⁹ F. BOHLMANN, H. BORNOWSKI and K.-M. KLEINE, *Chem. Ber.* **97**, 2135 (1964).

¹⁰ F. BOHLMANN, U. NIEDBALL and J. SCHNEIDER, *Chem. Ber.* **98**, 3018 (1965).

Finally, 60% Et₂O in light petrol. eluted a compound with an ene-diyne chromophore (λ_{max} 283, 268, 255 and 242 nm). However, insufficient material was obtained for characterization. The major MS peaks for the compounds III–IVc are shown in the Table 1. Further examinations of fresh extracts are in progress, in an attempt to identify the compounds whose structures have not been clarified.

TABLE 1. MS DATA FOR COMPOUNDS III, IVa, IVb AND IVc

<i>m/e</i>	III	Relative abundance (%)			<i>m/e</i>	III	Relative abundance (%)		
		IVa	IVb	IVc			IVa	IVb	IVc
41	36	33	100	93	127	36	15	31	60
43	10	100	72	29	128	28	23	59	91
					129	13	23	26	99
51			15	18					
53	13		15	18	139	69	11	35	21
55	14	25	70	58	140	55		17	
57		15	65	22					
					141	36	22	52	52
63	27		21	18					
65	21		15	31	152	100	16	19	23
67	14	12	30	52	153	82	19	22	29
69	10	17	70	60					
					165	85	11	17	18
71		10	45	12	166	28		10	10
74	24		29	10	167	19		16	18
75	30		20	14	169			66	13
77	46	14	30	44					
79	18	12	20	41	171		10		17
					177	18			
81	10	11	45	13	178	54			
83		11	39	18	179	32			
89	29		16	14	180	15			
91	21	17	27	52	189	15			
95			32	29					
97		10	36	12	191	25			
					192	30			
101	18		10	10	193	14			
102	10		25	18	195	10		11	
105			14	18					
108		10	25	27	207	19			
109			25	14	208	28			
114	25			17	222	54 M ⁺			
115	59	26	90	100					
116	13		16	35	238			15 M ⁺	
117		10	10	32	239		12		
					240				31 M ⁺
					282		10 M ⁺		

EXPERIMENTAL

Senecio jacobaea L. plants were collected near Moesgaard on clay slopes facing the sea at the beginning of July 1971. (A voucher specimen is retained in our laboratory.) The plants were washed, separated into roots, aerial parts and flowers, minced and extracted with light petrol. for 24 hr. The solvent was removed from the extracts by evaporation and the crude extracts weighed. Only the extract from the flowers showed any acetylenic compounds as assayed by UV. 7.6 kg flowers yielded 30.65 g crude extract. The extract was chromatographed on silica gel (Merck) columns made up in light petrol. Preparative TLC was performed on 2.5 mm thick layers of silica gel G (Merck), using light petrol. containing various proportions of Et₂O as eluent. NMR spectra were run in CDCl₃. MS were recorded on CEC 21-104 instrument with a direct inlet system, at a source temp. of 200°. The following amounts of the compounds were isolated. II, 0.5 mg; III, 0.5 mg; IVa, 60 mg; IVb, 35 mg.