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POLYACETYLENES OF *SOLIDAGO VIRGAUREA*: THEIR SEASONAL VARIATION AND NMR LONG-RANGE SPIN COUPLING CONSTANTS

JØRGEN LAM
Chemical Institute, University of Aarhus, 8000 Århus C, Denmark

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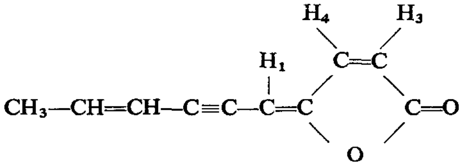
Abstract—Great variation in polyacetylene content with season was noted in this plant. The major compounds present are 2,8-*cis–cis*-matricaria ester (I), two matricaria-γ-lactones (II and III), and one lachnophyllum lactone (IV). Two epoxides and an acetylenic hydrocarbon are present in the roots, whereas no acetylenic compound could be detected in the aerial parts of the plants. The exo double bond *cis–trans* relationship between II and III was established from NMR long-range couplings in these and other protoanemonin derivatives.

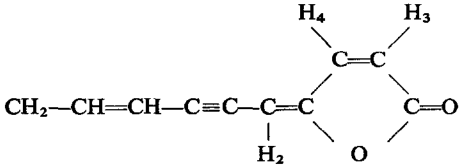
INTRODUCTION

EXAMINATIONS of Danish *Solidago virgaurea* plants collected within an area of 2500 m^2 in a fairly open beech forest did not reveal as much 2,8-*cis–cis*-matricaria ester as that reported for a Norwegian *Solidago virgaurea* by Sørensen.[1] The Norwegian plant contained 8 g/kg fresh root material, while in the Danish plants the maximum average amount per kg fresh root material is 558 mg (in December). The plants were collected month by month starting on 15 September (at the end of flowering) and repeated in the middle of October, November and December. In the succeeding year (1969) three collections were carried out at the end of April, in the middle of June, and in the beginning of August.

The acetylenes, I, II and IV, were isolated abundantly from the roots. They have earlier been reported to be present in Asteraea and Anthemideae.[2–5]

$$CH_3{-}\overset{cis}{CH{=}CH}{-}C{\equiv}C{-}C{\equiv}C{-}\overset{cis}{CH{=}CH}{-}COOCH_3 \qquad \text{(I)}$$


(II)


(III)

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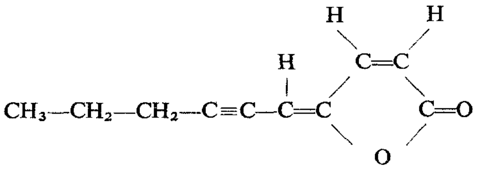
[1] D. HOLME and N. A. SØRENSEN, *Acta Chem. Scand.* **8**, 34 (1954).

[2] N. A. SØRENSEN and K. STAVHOLT, *Acta Chem. Scand.* **4**, 1080 (1950).

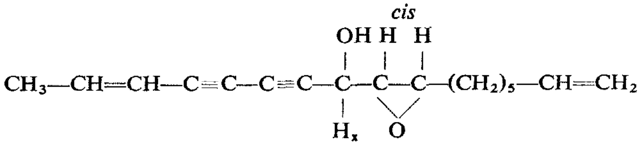
[3] P. K. CHRISTENSEN, *Structural and Spectroscopic Studies on Naturally Occurring Acetylenes of Composites*, Norges Tekniske Vitenskapsakademi, Trondheim 1959.

[4] F. BOHLMANN, H. BORNOWSKI and C. ARNDT, *Chem. Ber.* **98**, 2236 (1965).

[5] F. BOHLMANN and K.-M. KLEINE, *Chem. Ber.* **99**, 2096 (1966).

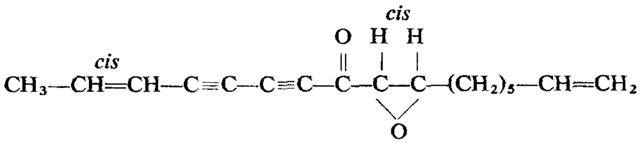


(IV)



(V)

$$CH_3-CH{=}CH-C{\equiv}C-C{\equiv}C-\underset{H_x}{\overset{OH}{C}}-\overset{H}{C}-\overset{H}{C}-(CH_2)_5-CH{=}CH_2 \quad (\text{cis};\ \text{epoxide } O \text{ bridging the } CH\text{–}CH)$$



(VI)

$$CH_3-\overset{cis}{CH{=}CH}-C{\equiv}C-C{\equiv}C-\overset{O}{\overset{\|}{C}}-\overset{H}{C}-\overset{H}{C}-(CH_2)_5-CH{=}CH_2 \quad (\text{cis};\ \text{epoxide } O \text{ bridging the } CH\text{–}CH)$$

RESULTS AND DISCUSSION

In October small shoots (1–5 mm long and with an average diameter of 1–3 mm) had been formed on the under-ground parts; 3 g of purple shoots were cut off and minced. They were shown to contain matricaria ester. The amounts of matricaria ester were determined to be 780 mg/kg fresh material in October, 1750 mg in November and 3060 mg in December. In April the shoots had developed to above ground parts and no acetylenic compounds could be detected except in the roots. It is emphasized that no sign of acetylenic substances other than matricaria ester could be detected in the extract from the purple shoots after separation on a silica column. In Table 1 are reported the amounts of the closely related acetylenes I–IV and V.

III was isolated in small amounts by elution from a silica column, appearing just after I and before IV, when eluted with light petroleum or a mixture of light petroleum and ether. The u.v. spectrum showed one broad peak at 343–348 nm. IV had a chromophore indicating

TABLE 1

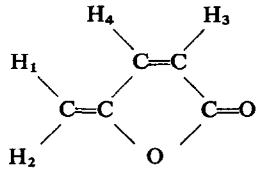
	Locality							
	Marselisborg							Svejbaek
	15 Sept. 1968	12 Oct. 1968	15 Nov. 1968	11 Dec. 1968	30 Apr 1969	17 June 1969	5 Aug. 1969	15 Oct 1968
	mg/kg fresh material (roots)							
I	68	36	418	558	112	445	229	79
II	159	214	138	312	188	159	218	254
III	2	7	10	0	10	0	0	23
IV	43	157	50	6	24	9	13	58
V	40	50	114	30	42	70	65	35

one double bond less than III showing a peak at 316–320 nm. II was the most polar compound eluted after IV and it showed the same u.v. spectrum as III. III may be an artefact produced from II by u.v. irradiation, although no acetylenic substance has been detected in the upper parts of the plants. From Table 1 it can be seen that the amount of III from plants grown in one locality (Svejbæk) is twice that of plants from another (Marselisborg) at the same time of year (mid October). In Svejbæk the plants were collected on open moor. In November the leaf-fall and in April the fact that there are no leaves on the trees may be the explanation of the relatively high amounts of III.

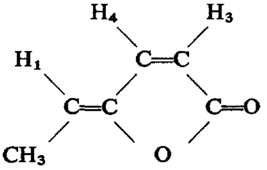
When irradiated with u.v. light II was transformed into III until a certain equilibrium had been reached; no attempts have been made to evaluate the proportions as the primary aim was to show that transformation occurs and to isolate and identify the acetylenic substance formed.

The *cis–trans* relationship of the exocyclic double bond in II and III was established by NMR spectroscopy (Table 2).

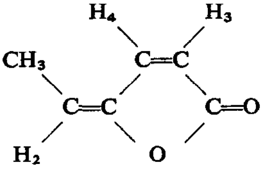
The long-range coupling constants J_{13} in II and J_{23} in III were determined to be 0·75 Hz and 1·60 Hz, respectively. Furthermore, the protons 1 and 4 in II show a change in chemical shift when the compound is transformed into III from 4·53 τ and 2·47 τ to 4·27 τ and 2·27 τ, respectively. In order to get more insight in the nature of these long-range couplings the constants were compared with the coupling parameters obtained from a complete computer refined analysis of the NMR spectrum of protoanemonin. The signs of the coupling constants in this compound are also given and were determined from spin tickling experiments[6] (see also Table 2).



Protoanemonin



Methyl protoanemonin A



Methyl protoanemonin B

The data obtained from the NMR spectra of the methyl protoanemonins A and B,* also being related to the naturally occurring compounds II and III, are given in Table 2. The assignment of the proton bands to the protons 1 and 2 in protoanemonin was based on a

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* Obtained as a mixture of *cis–trans* isomers according to Walton.[7]

[6] E. Freemann and W. A. Anderson, *J. Chem. Phys.* **37**, 2053 (1962).

[7] H. M. Walton, *J. Org. Chem.* **22**, 312 (1957).

TABLE 2. NMR CHEMICAL SHIFTS (τ, ppm) AND LONG-RANGE COUPLING CONSTANTS (Hz) IN PROTOANEMONIN DERIVATIVES

Compound	Solvent	$\tau(1)$	$\tau(2)$	$\tau(3)$	$\tau(4)$	J_{12}	J_{13}	J_{14}	J_{23}	J_{24}	J_{34}
Protoanemonin*	CS_2	5·15	4·90	3·85	2·57	−2·31	0·87	−0·46	1·80	−0·53	5·48
Methyl protoanemonin A†	$CDCl_3$	4·55		3·80	2·52		0·75	−0·40			5·55
Methyl protoanemonin B‡	$CDCl_3$		4·15	3·80	2·18				1·85	−0·75	5·60
II	CCl_4	4·53		3·75	2·47		0·75	−0·30			5·40
III	CCl_4		4·27	3·77	2·27				1·60	−0·60	5·40

* Root mean square (r.m.s.) error in line positions: 0·024.

† $J_{CH_3-H(3)} = -0{\cdot}70$ Hz.

‡ $J_{CH_3-H(3)} = -0{\cdot}65$ Hz.

comparison of the long-range couplings $^5J_{tt}$ and $^5J_{ct}$ with the corresponding coupling constants obtained from complete analysis of the proton spectra of butadienes.[8] Thus the suggested structures are in accordance with the longrange couplings J_{13} and J_{23} in II and III. It is seen that $^5J_{tt}$ is twice the order of magnitude of $^5J_{ct}$, in agreement with earlier results on butadienes.[8] The protons 1 and 4 in II and methyl protoanemonin A show almost the same chemical shift, whereas the corresponding protons H_2 and H_4, in the isomers III and methyl protoanemonin B, are shifted downfield by approximately the same amount. Finally, it is observed that the figures for H_1 and H_2 in protoanemonin agree well with the data found for the corresponding protons II, III, and the methyl protoanemonins.

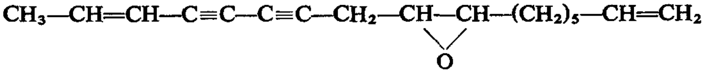
According to Bohlmann,[4] II exhibits a peak in the i.r. spectrum at about 945 cm^{-1} while III does not, which is in agreement with our observations. Although the u.v.-spectra are the same for II and III, it is possible to distinguish them by chromatography and u.v. inspection as they are well separated on a silicagel column.

The substance produced by u.v. irradiation, III, and the corresponding naturally occurring compound were identical by TLC.

An acetylenic substance V with an ene-diyne chromophore (λ_{max} 284, 268, 254, 241·5 and 230 nm) is identical with that described by Bohlmann.[5] It occurs in *Anthemis rudolfiana* (Anthemideae) together with 2,8-*cis–cis*-matricaria ester, matricaria-γ-lactone, and matricaria acid.

A doublet corresponding to one proton at 5·70 τ is most likely due to a proton, H_x, situated between an epoxide group and an acetylenic bond, and a multiplet at 7·0 τ contains the epoxide protons; the OH-group proton gives a signal at 7·6 τ; spin decoupling of the proton H_x results in a doublet with a coupling constant of 4·2 Hz for the epoxide protons. The *cis*-coupling constant of a *cis*-epoxide is of that order, while a *trans*-epoxide shows a coupling constant of about 2 Hz.[9] The double bond protons were also shown to be *cis* in agreement with the i.r. spectrum. The u.v., i.r., and NMR spectra are in agreement with data reported by Bohlmann.[5]

When oxidized with manganese dioxide the epoxide changes to another substance with an extended chromophore (λ_{max} 322, 304, 287, 271, 241 and 233 nm) in ether, and an NMR spectrum where the proton H_x and the OH-proton have disappeared. A doublet at 6·54 τ. One of the epoxide protons shows a coupling constant of 4·2 Hz in accordance with that obtained from the spin decoupling experiment mentioned above. The oxidation product appears to be VI.



$$CH_3{-}CH{=}CH{-}C{\equiv}C{-}C{\equiv}C{-}CH_2{-}\underset{\diagdown O \diagup}{CH{-}CH}{-}(CH_2)_5{-}CH{=}CH_2 \qquad \text{(VII)}$$

$$CH_3{-}CH{=}CH{-}C{\equiv}C{-}C{\equiv}C{-}CH_2{-}CH{=}CH{-}(CH_2)_5{-}CH{=}CH_2 \qquad \text{(VIII)}^{10}$$

Two polyacetylenes with ene-diyne chromophores were detected in the early fractions from the silica column indicating relatively non-polar substances. They were eluted together, but would be fairly well separated by repeated chromatography. VIII is the least polar and an insufficient amount of this compound was isolated to allow complete characterization. An NMR spectrum of VII (not quite pure) indicated epoxy-protons, vinyl protons, and *cis*-double bond protons as well as a double doublet due to $CH_3{-}CH{=}CH{-}$.

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[8] A. L. SEGRE, L. ZETTA and A. DICORATO, *J. Mol. Spectry* **32**, 296 (1969) and refs. cited.

[9] C. A. REILLY and J. D. SWALEN, *J. Chem. Phys.* **35**, 1522 (1961).

[10] F. BOHLMANN, H. MÖNCH and U. NIEDBALLA, *Chem. Ber.* **99**, 586 (1966).

Table 3. Mass spectral data for the compounds V, VI, VII, and VIII

	m/e	Relative abundance (%)			
		V	VI	VII	VIII
	39	62	55	60	28
	41	100	100	100	55
	43	33	40	26	
	51		18	35	18
	53	20	18	32	14
	54	39	20		18
	55	76	80	87	23
	57	33	35	32	
	63	35	19	38	20
	65			26	19
	67	72	45	53	33
	69		38	21	
	71	84			
	77		28	80	39
	78			30	
	79	22	28	38	28
	81	27	20	25	14
	83	13	25		
	89	65	18	22	18
	90	51			
	91	10	18	60	35
	93	14		38	
	102		20		10
	103			49	13
	105			25	10
	109	9			
	115	3		87	65
	116				22
	117	6	45	63	18
	118	8			
	119	5			
	121	6			
	127				26
	128	3		23	100
	129			26	50
	131			24	
	141				33
	143				45
	145	2		34	
	159		5	21	
	173		10		
	174		5		
	225				0·4
VIII M^+	226				0·6
	240	0·5			
	241			1·0	
VII M^+	242			3·8	
VI M^+	256		3·5		
V M^+	258	0·3			

Mass spectra of V, VI, VII, and VIII were obtained by combined gas chromatography–mass spectroscopy. The molecular peaks were: 258, 256, 242 and 226 *m/e*, respectively, in good agreement with the formulae given (see also Table 3).

EXPERIMENTAL

Apparatus

The spin tickling experiments were performed on a Varian HA-100 spectrometer equipped with a Varian Spectro system 100. Calculations of NMR spectral parameters were performed at N.E.U.C.C., Copenhagen. The mass spectral data came from a Perkin–Elmer 880 gas chromatograph equipped with a 1 m 2% SE 52 column connected with a Hitachi–Perkin–Elmer RMU-6D mass spectrometer, ionizing voltage 70 eV. The irradiation of II was carried out in a Rayonet Type RS preparative photochemical reactor RPR 208 at 3500 Å.

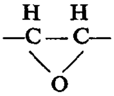
Shoots from *Solidago* roots were cut off in October, November and December. They were minced in a mortar after addition of dry Na_2SO_4 under light petroleum and extracted repeatedly with this solvent and eventually with ether. The extracts were chromatographed on silica gel columns. Only 2,8-*cis–cis*-matricaria ester could be isolated from the shoots. Immediately after each collection fresh *root* material was minced and extracted repeatedly with light petroleum (b.p. below 50°) and ether until no u.v. absorption could be detected above 260 nm in the extracts. The extracts were concentrated and poured onto silica columns and the concentrations of the various eluates determined from their u.v. absorption. There was good agreement between the amounts determined in this way and the amounts isolated.

I, II, and IV were isolated and analyzed by their spectra. Comparison with data available in literature for these compounds ensure full characterization.[3,4]

Irradiation of II

50 mg portions of II dissolved in a mixture of 35 ml of ether and 35 ml of light petrol were irradiated for about 30 min in pyrex tubes with light of wavelength 3500 Å. An equilibrium of the *cis*- and *trans*-forms at the exocyclic double bond resulted, whereas only a little change had occurred at the *cis* double bond neighbouring the CH_3-group. For characterization via the NMR and the i.r. spectra see above.

Oxidation of V

70 mg of V in 50 ml of ether were oxidized catalytically with MnO_2 by stirring at room temp. for 15 min. After separation by chromatography on silica gel 47 mg of VI were obtained as a pure compound (TLC and GLC). *I.r.-spectrum.* —C≡C— 2155 and 2225 (very strong) cm^{-1} ≡C>C=O (ketone) 1665 and 1680 cm^{-1}, —CH=CH_2 990 and 910 cm^{-1},  $-\overset{H}{C}-\overset{H}{C}-$ (epoxide, O bridging) 860 cm^{-1}. *Mass spectrum*: see Table 3.

Acknowledgements—The author is greatly indebted to mag. scient. H. J. Jakobsen, at this institute, for the complete analysis of the spectra of protoanemonin including the relative sign determination by double resonance and the discussions of the structures II, III and V based on these data. I am grateful to Dr. P. E. Brandt, Grindstedværket, Brabrand, for the mass spectra. The experimental assistance of Miss Hanne Weiling is gratefully acknowledged, and Mr. D. Drake, M.Sc., University of Manchester, is thanked for the linguistic criticism of the manuscript.