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Spectral and Oxidation Studies on Matricaria Ester (*n*-Decadiene-2,8-Diyne-4,6-oic Acid Methyl Ester)

RALPH T. HOLMAN* and NILS ANDREAS SØRENSEN

Biokemiska Avdelningen, Medicinska Nobelinstitutet, Stockholm, Sweden, and Institutt for Organisk Kjemi, Norges Tekniske Högskole, Trondheim, Norway

In 1941 Sørensen and Stene [1] reported the isolation of a highly unsaturated ester from the flowers of *Matricaria inodora L.* They found that the ester conformed to the empirical formula $C_{11}H_{10}O_2$, and that upon hydrogenation, it absorbed 6 moles of hydrogen to form methyl decanoate. In consequence of the identity of degradation products, the high molecular exaltation of the ester, and by analogy with the ester isolated from *Lachnophyllum gossypinum* by Wiljams, Smirnow and Goljmow [2], the matricaria ester was tentatively assigned the formula $CH_3CH = CH - C \equiv C - C \equiv C - CH = CHCOOCH_3$.

At the time the initial work was done, facilities for determination of ultraviolet absorption spectra were not available. It was believed that a study of the absorption characteristics of this highly unsaturated ester and its acid should be of help in elucidating its structure. It was with that end in mind that the present study was made. While the preparations were available additional studies were made concerning the oxidation of this highly unsaturated ester.

EXPERIMENTAL

The spectral measurements were made on freshly prepared samples shipped in vacuum ampules packed in solid carbon dioxide from the laboratory in Trondheim to Stockholm. Less than 36 hours elapsed between preparation and spectral examination with the Beckman spectrophotometer. All samples were recrystallized from pentane immediately before use. Oxidation studies were made upon 100 millimole samples under air at 37° in the Warburg apparatus, and samples were removed for spectral measurements at appropriate intervals of oxygen uptake. The procedure used has been described previously [3].

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* National Research Council Fellow (U.S.A.) in Physiological Chemistry 1946–47 and American-Scandinavian Foundation Fellow 1947–48. Present address: Department of Biochemistry and Nutrition, Texas A & M College System, College Station, Texas U. S. A. Acknowledgement is made to the Nutrition Foundation whose grant-in-aid made this work possible.

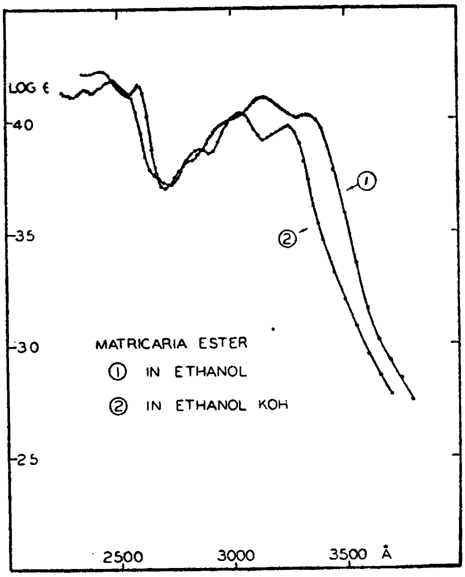

Fig. 1. Ultraviolet absorption spectra of matricaria ester. (1) in ethanol, (2) in alkaline ethanol.

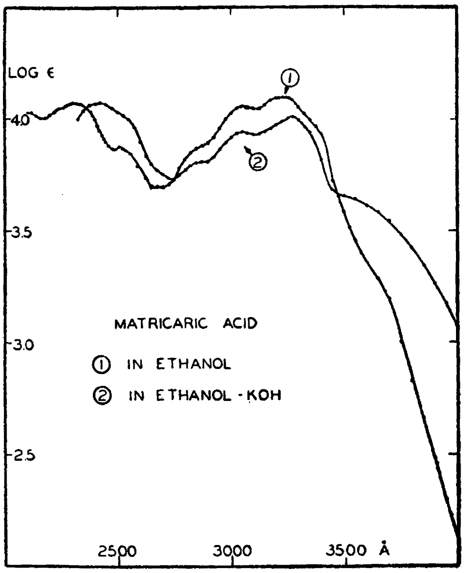

Fig. 2. Ultraviolet absorption spectra of matricaric acid. (1) in ethanol, (2) in alkaline ethanol.

RESULTS AND DISCUSSION

The ultraviolet absorption spectra of matricaria ester and related compounds exhibit very interesting and unusual properties. The spectra of matricaria ester in ethanol and alkaline ethanol, shown in Figure 1, have two families of absorption maxima. In alkaline solution these maxima lie at shorter wavelengths (see Table 1). The spectral shift as a consequence of alkaline treatment is more pronounced in the case of matricaric acid, whose spectra are shown in Fig. 2. A similar study was made with 3,8-dimethyldecadiene-2,8-diyne-4,6 (Fig. 3) which was prepared by C. M. Haug for comparison with matricaria ester. The spectra of this substance in ethanol and alkaline ethanol are almost identical, indicating that the shifts in spectra of the matricaria ester and acid are associated with the effect of alkali upon the ester and acid groups rather than upon the conjugated diene-diyne system.

The spectra of matricaria ester and 3,8-dimethyldecadiene-2,8-diyne-4,6 in non-polar solvents are shown in Fig. 4. Although the absorption maxima of the latter compound occur at lower wavelengths (see Table 1), the spectra show considerable similarity. Theoretical considerations, to be published separately, have led Sørensen to conclude that the two compounds have the

Table 1. Absorption maxima of matricaria ester, matricaric acid and 3,8-dimethyldecadiene-2,8-diyne-4,6.

Substance	*In ethanol*		*In ethanol-KOH*		*In hydrocarbon*	
	λ	ε	λ	ε	λ	ε
Matricaria ester	3330 Å	10 330	3250 Å	9 376	3360 Å	12 900
	3145	12 550	3040	8 147	3140	15 540
	2970 ~	9 680	2860	7 550	3010 ~	12 490
	2830 ~	6 730				
	2590	14 300			2590	23 060
	2470	15 230	2420	16 900	2460	25 380
	2340	13 770			2320	22 200
Matricaric acid	3600 ~	2 259	3600 ~	4 150		
	3400 ~	8 690				
	3250	12 560	3275	10 120		
	3050	11 400	3050	8 730		
	2875 ~	7 551	2875 ~	6 383		
	2500	7 780	2550 ~	9 728		
	2310	11 670	2425	11 770		
3,8-Dimethyldeca-diene-2,8-diyne-4,6	3070	10 590	3080	11 040	3085	11 120
	2890	13 370	2890	14 060	2900	14 450
	2730	9 530	2730	10 070	2740	10 220
	2590	5 530	2590	5 850	2600	5 875
	2310	26 310			2310	29 380
					2280	29 040
					2220	27 100

$\varepsilon = (\log_{10} I_0/I)/cl$, when c = mole per liter and $l = 1$ cm.
~ denotes inflection point.

same conjugated structure, $-CH=CH-C\equiv C-C\equiv C-CH=CH-$, and that the tentative formula is correct.

The autoxidation of matricaria ester was studied, using freshly recrystallized ester. The oxygen uptake, shown in Fig. 5, indicates that the reaction follows a diphasic course. The first phase, probably involving the addition a mole of oxygen, proceeded at 0.09 moles oxygen per mole ester per hour. The second phase continued at the rate of 0.024 M/M/hr until nearly one mole of oxygen was absorbed. The maximum rate of oxygen uptake of a nearly pure sample of methyl docosahexaenoate supplied by Dr. D. A. Sutton was found to be 0.12 M/M/hr. This ester contains the

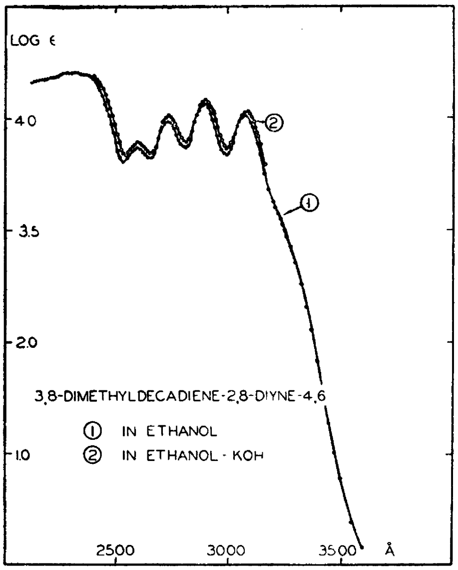

Fig. 3. Ultraviolet absorption spectra of 3,8-dimethyldecadiene-2,8-diyne-4,6. (1) in ethanol, (2) in alkaline ethanol.

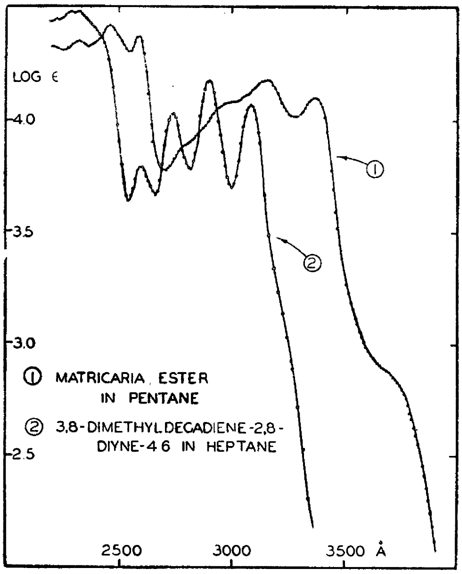

Fig. 4. Ultraviolet absorption spectra. (1) matricaria ester in pentane, (2) 3,8-dimethyl decadiene-2,8-diyne-4,6 in heptane.

same total unsaturation as does matricaria ester, but in the form of six isolated double bonds. The matricaria ester oxidizes at a rate comparable to that of linoleic acid[4].

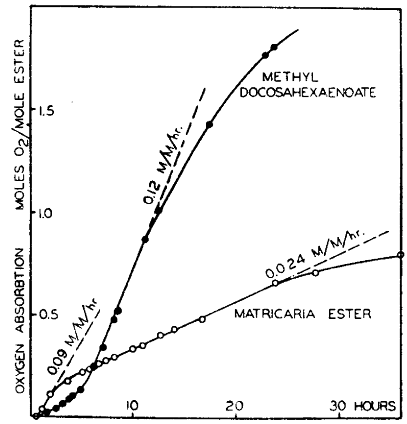

Fig. 5. The course of the oxidation of matricaria ester and methyldocosahexaenoate.

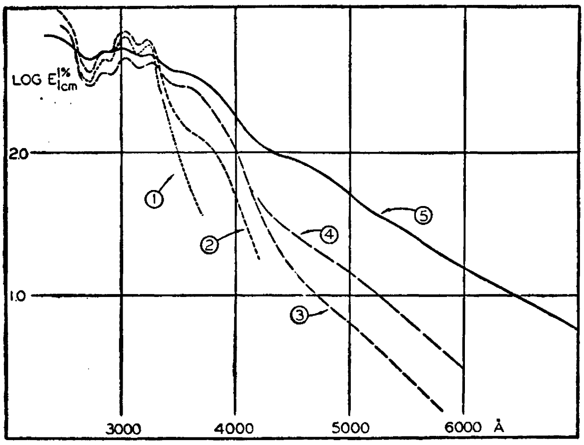

Fig. 6. Ultraviolet spectra of oxidized matricaria ester in alkaline ethanol. (1) fresh ester, (2) 0.08 M/M, (3) 0.1 M/M, (4) 0.26 M/M, (5) 0.80 M/M.

As the oxidation of the ester proceeds, the color of the sample progressively deepens, and the oxidized material loses its solubility in alcohol or ether. For this reason, the changes in the spectrum of the ester could not be followed during the oxidation. The oxidized ester, however, was soluble in alcoholic potassium hydroxide, permitting examination of the oxidized ester's spectrum in alkaline ethanol. Figure 6 shows the spectra of matricaria ester in alkaline solution during the course of the autoxidation. The effect of alkali upon the fresh ester is to move the absorption bands away from the visible, and eventually after some hours, to obliterate the fine structure. However, the spectra of oxidized matricaria ester in alkaline ethanol showed, not so much a depression of the principal bands, but a progressive increase in absorption toward the visible region. In this broad increase in absorption, a definite band is distinguishable at about 3550 Å. This band is the first to develop, the visible absorption increasing later. These two types of absorption, shown in Fig. 7, correspond to the phases of oxygen uptake mentioned previously. It appears that the 3550 Å chromophore is associated with the primary oxidation product.

SUMMARY

1. Ultraviolet absorption spectra of matricaria ester, matricaria acid and 3,8-dimethyldecadiene-2,8-diyne-4,6 are given for polar and non-polar solutions.

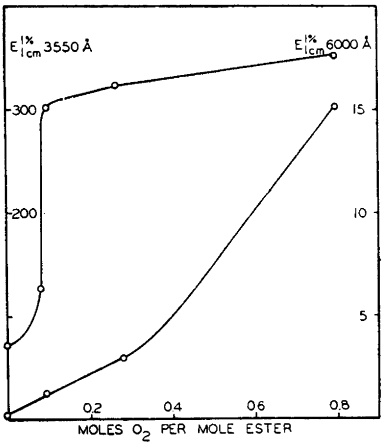

Fig. 7. Chromophore development during course of autoxidation of matricaria ester.

2. The similarity of absorption spectra of matricaria ester and 3,8-dimethyldecadiene-2,8-diyne-4,6 indicates that these contain similar conjugated unsaturated structures and that matricaria ester is *n*-decadiene-2,8-diyne-4,6-oic acid methyl ester.

3. Autoxidation of matricaria ester is extremely rapid and proceeds in two stages. A comparison of the rate of oxygen uptake of matricaria ester and methyldocosahexaenoate is made.

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