

length absorption had shifted to longer wave-lengths with stronger intensity while the short wave-length absorption ($\sim 2570 \text{ \AA}$) had undergone a hypsochromic shift with lower intensity. This phenomenon was further investigated, and it turned out that on dissolving *cis:cis* matricaria acid in a solvent containing water, in this case 95% ethanol, the rearrangement free acid \rightarrow lactone took place spontaneously. In absolute ethanol ($\sim 99.8\%$) the speed of reaction was very much slower.

A solution of the free acid in dry tetrahydrofuran was stable and the UV-absorption was quite similar to a solution in hexane. Addition of distilled water to the tetrahydrofuran immediately caused rearrangement to the lactone.

Working in a mixture of tetrahydrofuran and buffers (1:1) the reaction took place with a measurable speed in the interval $\text{pH} \sim 4.5-11$. Above $\text{pH} \sim 11$ also other reactions occurred and the product was no longer pure. Measurement of reaction velocities by means of UV-absorption was impossible.

In the interval $\text{pH} \sim 6-11$ the rate of reaction was approximately constant. The reaction appeared to be of first order with half-times of ~ 3.5 min at 30°C and ~ 11 min at 20°C . Below $\text{pH} \sim 6$ the rate decreased rapidly.

The same rearrangement in water-containing solvents has been followed starting

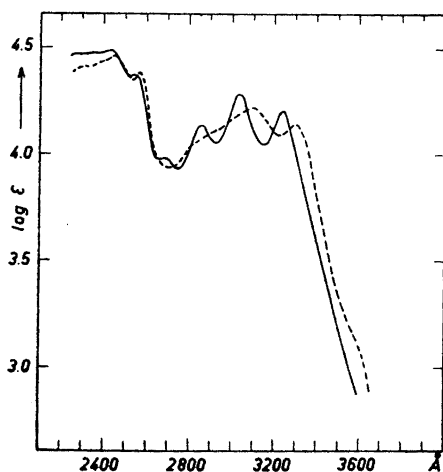


Fig. 1. 2-*trans* Matricaria acid, — — — in dry tetrahydrofuran; — in tetrahydrofuran-water (10:1).

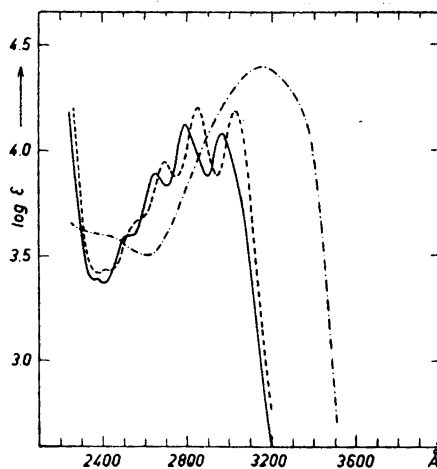
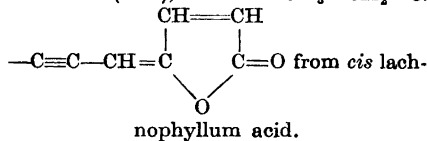


Fig. 2. *trans* Lachnophyllum acid, — — — in dry tetrahydrofuran; — in tetrahydrofuran-water (10:1); — — — $\text{CH}_3-\text{CH}_2-\text{CH}_2$



with *cis* lachnophyllum acid (III, $\text{R} = \text{CH}_3-\text{CH}_2-\text{CH}_2-\text{C}\equiv\text{C}-$). According to Ref.³ it also takes place with *cis* dehydro matricaria acid (III, $\text{R} = \text{CH}_3-\text{C}\equiv\text{C}-\text{C}\equiv\text{C}-$) at $\text{pH} = 8.4$. Other substances have not yet been tried.

When the rearrangement was followed in the UV-recorder with rapid successive scannings of the spectrum, it turned out that with the *cis:cis* matricaria acid no direct transformation from the free acid spectrum to the lactone spectrum took place, but some intermediate absorption with more pronounced fine structure (Fig. 3, curve 1) was observed. The transformation from the normal free acid spectrum to this spectrum took place in less than 0.5 min.

In order to be able to make a reasonable guess as to the origin of the absorption of this compound, some 2-*trans* matricaria acid was dissolved in tetrahydrofuran with water. This acid is incapable of forming a lactone for steric reasons and gave immediately after having been dissolved (< 0.5 min) a spectrum entirely different

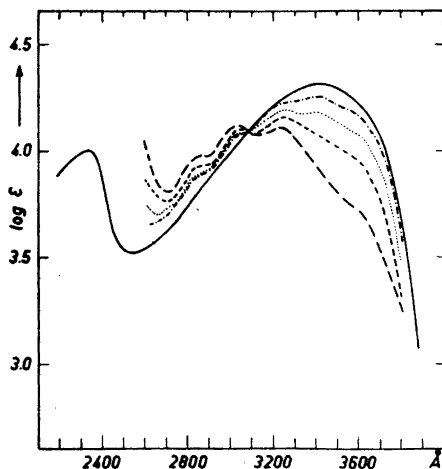


Fig. 3. Rearrangement of di *cis* matricaria acid in 95 % ethanol. Curve 1: --- 0.5–3.5 min after dissolving the acid, start at long wavelengths. Curve 2: ——— 80 min after dissolving the acid, total lactone formation. Other curves measured at intermediate times.

from that of the acid dissolved in hexane or dry tetrahydrofuran. In these two solvents the spectrum of the 2-*trans* acid (Fig. 1) was very similar to the spectrum of both the 2-*trans* and the 2-*cis*-ester with no marked fine structure in the long wavelength area (2 800–3 400 Å). When dissolved in tetrahydrofuran with water (10:1) a marked fine-structure developed with bands at 2 850, 3 035 and 3 240 Å (Fig. 1). The 2-*trans* lachnophyllum acid gave the same overall picture with a shift from 2 690, 2 850 and 3 025 Å in dry tetrahydrofuran to 2 645, 2 790 and 2 965 Å in tetrahydrofuran-water (10:1) (Fig. 2).

The substances *trans* (HC=C-CH=CH-COOH) and *trans* (-C=C-CH=CH-COOH)₂ gave the same shift to shorter wavelengths, although less pronounced. When 2-*cis*-matricaria acid is dissolved in 0.01 N ethanolic H₂SO₄, there is no formation of the fine-structure spectrum.

If samples are withdrawn at certain time intervals from a solution of the *cis*-acid in 95 % ethanol the reaction can be stopped with acid. Analysis of these samples in

UV now gives as result a set of curves where the intermediate curves between pure acid and pure lactone are mixtures of the normal acid spectrum and the lactone spectrum.

At present it is not possible to give a detailed reaction mechanism, but from the spectral studies two general routes are possible:

- A: Fine-structure complex \rightleftharpoons free acid
 \rightarrow lactone
 B: Free acid \rightleftharpoons fine-structure complex
 \rightarrow lactone

The choice between the two must await more detailed studies, the most probable is apparently B. If, in B, the equilibrium acid \rightleftharpoons complex is over to the right, there would be an apparent isosbestic point⁴ in the UV-curves from the reaction fine-structure complex \rightarrow lactone. (Fig. 3).

Holman and Sørensen⁵ reported in 1950 some spectral and oxidation studies on matricaria ester and the free acid. Their curve for the UV-absorption of the acid in ethanol can now be interpreted as being the curve for a mixture of the free acid and the lactone formed from it. The sharp maximum at \sim 2 580 Å in the pure free acid been reduced and indicates a fairly large amount of lactone formation. The maximum at 3 250 Å corresponds to the rapidly developed maximum in solvents containing water.

This work is in progress and further results will be published elsewhere.

The author thanks Prof. N. A. Sørensen for his interest and *Norges Teknisk-Naturvitenskapelige Forskningsråd* for financial support.

1. Sørensen, N. A. and Stavholt, K. *Acta Chem. Scand.* **4** (1950) 1080.
2. Christensen, P. K. *Det 9. Nordiske Kemikermøde*, Aarhus 1956.
3. Christensen, P. K., Sørensen, N. A., Bell, I., Jones, E. R. H. and Whiting, M. C. *Festschrift Proj. Dr. Arthur Stoll*, Basel 1957, p. 545.
4. Schläfer, H. L. and Kling, O. *Angew. Chem.* **68** (1956) 667.
5. Holman, R. T. and Sørensen, N. A. *Acta Chem. Scand.* **4** (1950) 416.

Received March 12, 1957.