## SHORT COMMUNICATIONS

# Studies on Chrysanthemate Derivatives. II.[1] Pyrolysis of Pyrethrin-I

Yasuo Nakada, Yasuo Yura, and Keisuke Murayama
*Central Research Laboratories, Sankyo Co., Ltd., Hiromachi, Shinagawa-ku, Tokyo*

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Five compounds were obtained by the pyrolysis of allethrin.[2] In this communication we wish to report a new product obtained by the pyrolysis of pyrethrin-I.

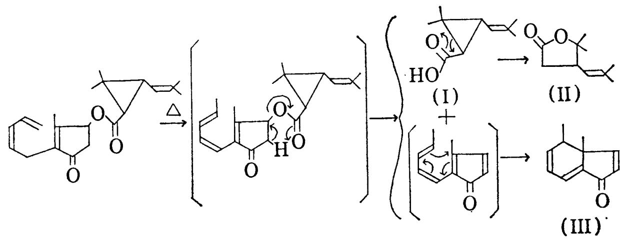
Pyrethrin-I, cinerin-I, and jasmolin-I were advantageously separated from the mixtures extracted from pyrethrum flowers,[3] using a special column chromatography on silica gel impregnated with silver nitrate. Pyrolysis of pyrethrin-I was carried out at 400°C as reported previously.[2] The reaction products were separated into an acidic and a neutral fraction by alkaline extraction.

The acidic fraction gave chrysanthemic acid (I) as the only product.

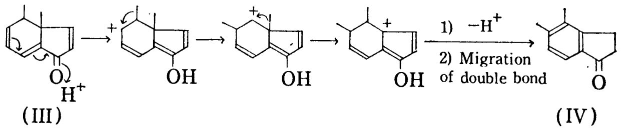
The neutral fraction consisted of pyrocin (II) and a new compound (III) separated by column chromatography on silica gel. Compound III revealed the following spectral data; *m/e* 160 ($M^+$) and 145 (M-15); IR, $\nu_{max}$ cm$^{-1}$: 1680 and 1640; UV, $\lambda_{max}^{EtOH}$ m$\mu$ (log $\varepsilon$): 230 (3.50) and 319 (3.64); NMR,[4] a doublet methyl at 9.39 (3H; $J$=7.1 Hz), a singlet methyl at 8.87 (3H), a multiplet proton on a tertiary carbon at 7.73 (1H), and five olefinic protons at 3.70—3.90 (m, 3H), 3.41 (ddd, 1H; $J$=1.0, 2.1, and 5.0 Hz), and 2.55 (dd, 1H; $J$=1.0 and 6.0 Hz). Heating compound III with concentrated hydrochloric acid afforded a white crystalline substance, mp 84—86°C, which was designated as 4,5-dimethyl-1-indanone(IV) on the basis of the following mass, IR, UV, and NMR spectral data and by comparison with those of the independent synthetic product prepared from *o*-xylene using the method of Hart and Teble;[5] *m/e* 160 ($M^+$), 145 (M-15), and 132 (M-28); IR, $\nu_{max}$cm$^{-1}$: 1709 and 818 (1,2,3,4-tetrasubstituted phenyl); UV, $\lambda_{max}^{EtOH}$m$\mu$ (log $\varepsilon$): 258 (4.19) and 292 (3.46); NMR,[6] two singlet methyls at 7.80 (3H) and 7.67 (3H), two multiplet methylenes at 7.48 (2H) and 7.09 (2H), and two aromatic protons centered at 2.95 (d, 1H; $J$=4.0 Hz) and 2.65 (d, 1H; $J$=4.0 Hz).

From these results compound III is presumed to be 4,5-dimethyl-bicyclo[4.3.0]nona-2,6,8-triene.

We propose that the reaction mechanisms for the pyrolysis of pyrethrin-I and for the acid catalyzed rearrangement of compound III to compound IV take place as shown in Scheme 1 and 2, respectively.



Scheme 1



Scheme 2

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[1] The previous paper[2] is regarded as Part I of this series.

[2] Y. Nakada, Y. Yura, and K. Murayama, This Bulletin, **44**, 1724 (1971).

[3] R. M. Sawicki and E. M. Thain, *J. Sci. Food Agr.*, **12**, 137 (1961).

[4] NMR spectra were determined at 60 MHz in $CCl_4$ and chemical shift is expressed in $\tau$ from internal TMS.

[5] R. T. Hart and R. F. Teble, *J. Amer. Chem. Soc.*, **72**, 3286 (1950).

[6] NMR spectra were determined at 100 MHz in $CCl_4$.