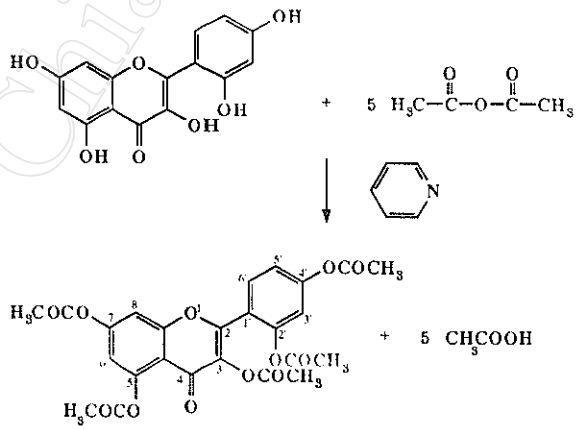
CHAPTER IV

RESULTS AND DISCUSSION

Three morin esters, morin-3,5,7,2′,4′-pentaacetate, morin-3,7,2′,4′-tetrapalmitate and morin-3,5,7,2′,4′-pentanicotinate, were synthesized in this study. Each reaction for the synthesis of these compounds are discussed as follows.

MORIN-3,5,7,2′,4′-PENTAACETATE

Morin-3,5,7,2′,4′-pentaacetate was synthesized by acetylation of morin with acetic anhydride, using pyridine as catalyst. Over all reaction is,



The mechanism of reaction is shown in figure 3.

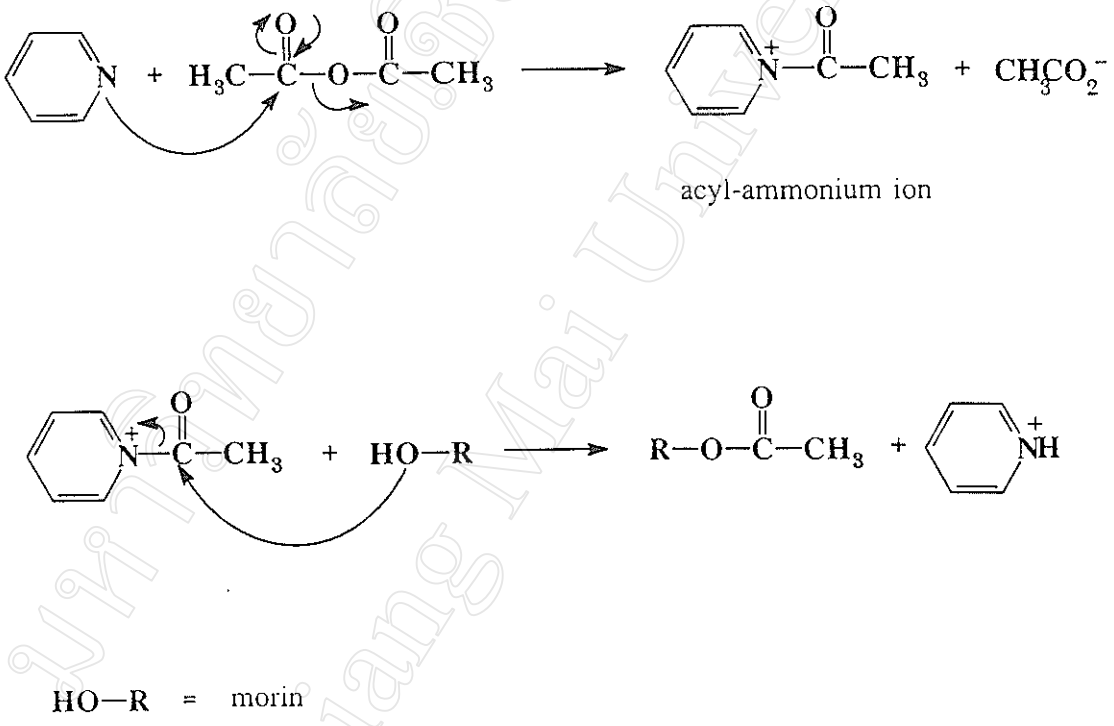


Figure 3 The mechanism of the formation of morin-3,5,7,2′,4′-pentaacetate.

The structure of morin-3,5,7,2′,4′-pentaacetate was confirmed by UV-Visible spectrum, IR spectrum, ^{1}H-NMR spectrum, ^{13}C-NMR spectrum and mass spectrum.

The UV-Visible spectrum (see page 67) showed λmax at 286.51 nm and 248.84 nm, that represented for aromatic chromophore.

The IR spectrum (see page 71) showed a C=O harmonic vibration (overtone) peak at 3530.28 cm^{-1}. A peak at 1776.32 cm^{-1} assigned for C=O stretching vibration of ester. A peak of C=O stretching vibration of cyclic conjugated ketone appeared at 1654.27 cm^{-1}. The peaks at 1370.91 cm^{-1} and 1193.36 cm^{-1} represented for C-H deformation and C-O stretching vibration of acetyl groups, respectively.

The ^{1}H-NMR spectrum (see page76-78) showed the peaks at δ 2.175 (s, 3H), 2.241 (s, 3H), 2.327 (s, 3H), 2.337 (s, 3H) and 2.434 (s, 3H), which represented for acetyl protons. The peaks with meta coupling at δ 6.888 (d, 1H, J=2.14), 7.116 (d, 1H, J=2.14) and 7.232 (d,1H, J=2.14) assigned for protons at 8, 6 and 3′ position, that can not be specified the certain position. The peak of H-6′ that was ortho coupling with H-5′, appeared at δ 7.576 (d, 1H, J=8.55). The peak at δ

7.161 (q, 1H, J=2.14; 2.14; 8.55) was H-5′ that was ortho coupling with H-6′ and meta coupling with H-3′.

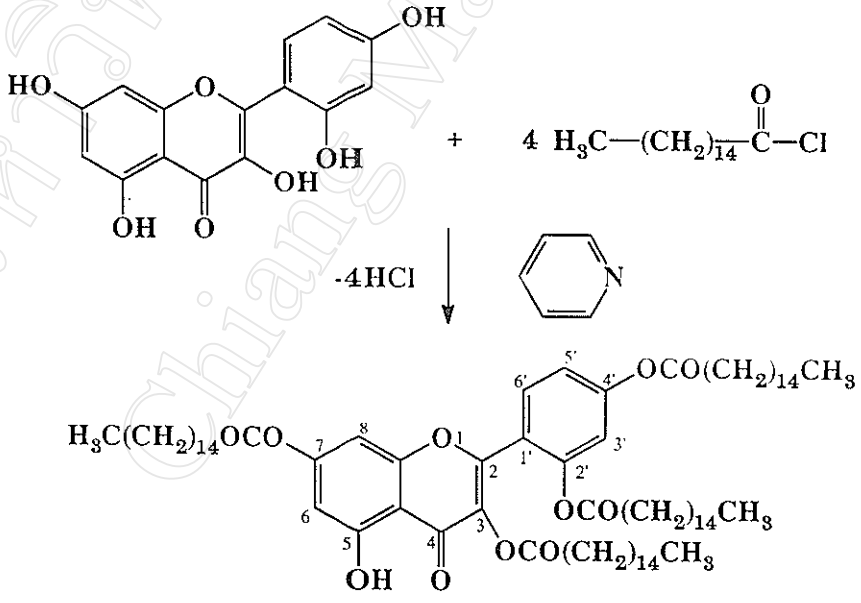
The ^{13}C-NMR spectrum (see pages 86, 87) showed the peaks at δ 20.202 (1C), 20.996 (1C), 21.018 (1C) and 21.116 (2C) which represented for methyl carbons of acetyl groups. The peaks at δ 109.015 (1C), 114.032 (1C), 115.038 (1C), 117.370 (1C), 119.395 (1C), 119.873 (1C), 130.719(1C), 134.982 (1C), 149.002 (1C), 150.514 (1C), 153.006 (1C), 153.094 (1C), 154.271 (1C) and 157.262 (1C) were assigned for carbon atoms of morin part, excepted carbonyl carbon atom. The peaks at δ 167.609 (1C), 167.795 (1C), 168.466 (1C), 168.713 (1C), 169.285 (1C), and 169.770 (1C) were carbonyl carbon atoms. The peak at 77.000 was the residual proton of deuterochloroform.

The mass spectrum (see pages 89, 90) showed molecular ion (M^+) peak at m/e = 513 (0.96 %) [calculated molecular weight of morin-3,5,7,2′,4′-pentaacetate =512.44]. Intensity of molecular ion peak was very low, because the C-O bond of carboalkoxy groups were easily broken down. The peaks at m/e 470, 428, 386, 344 and 302 represented

for $M^+ - COCH_3 + H^\cdot$, $M^+ - 2COCH_3 + 2H^\cdot$, $M^+ - 3COCH_3 + 3H^\cdot$, $M^+ - 4COCH_3 + 4H^\cdot$ and $M^+ - 5COCH_3 + 5H^\cdot$, fragment ions, respectively.

MORIN-3,7,2′,4′-TETRAPALMITATE

Morin-3,7,2′,4′-tetrapalmitate was synthesized by esterification of morin with palmitoyl chloride. Pyridine was added to react with hydrochloric acid generated in ester-forming reacton.Overall reaction is,



The mechanism of reaction is showed in figure 4. The hydroxyl group at 5-position did not react because of strong intramolecular hydrogen bonding and steric hindrance of the carbonyl group.

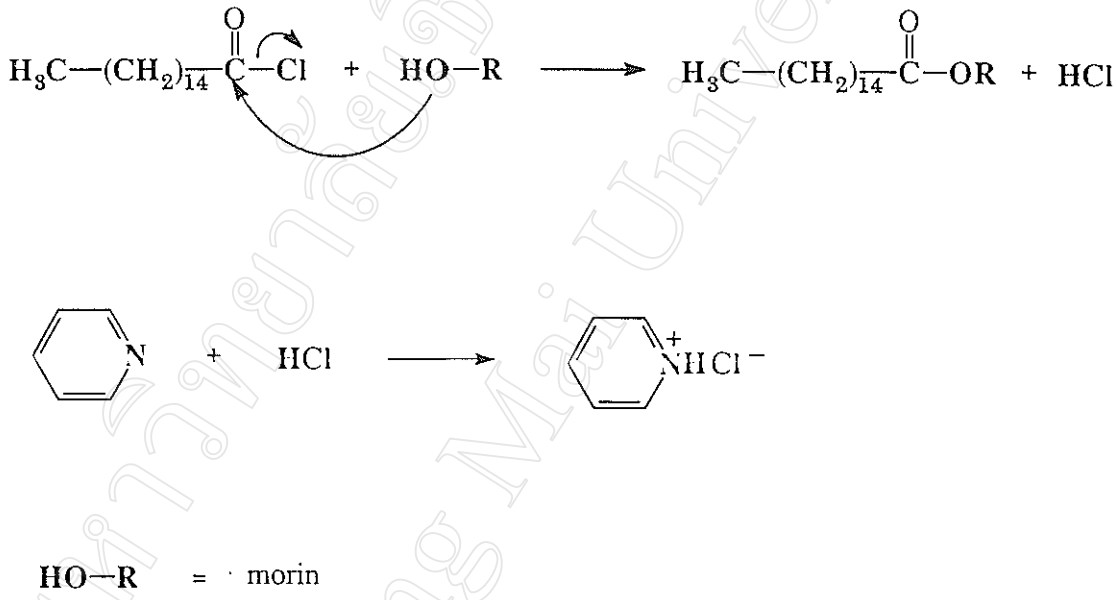


Figure 4 The mechanism of the formation of morin-3,7,2′,4′-tetrapalmitate.

The structure of morin-3,7,2′,4′-tetrapalmitate was confirmed by UV-Visible spectrum, IR spectrum, ^{1}H-NMR spectrum and mass spectrum.

The UV-Visible spectrum (see page 68) showed λmax at 331.16 nm and 261.40 nm, that represented for aromatic chromophore.

The IR spectrum (see page 72) showed the peak O-H stretching vibration at 3450 cm^{-1}. The peaks at 2900 cm^{-1} and 2850 cm^{-1} represented for C-H stretching vibration of methyl and methylene groups, respectively. The strong peak at 1765 cm^{-1} assigned for C=O stretching vibration of ester. The peak of C=O stretching vibration of cyclic conjugated keton appeared at 1655 cm^{-1}.

The ^{1}H-NMR spectrum (see pages 79-81) showed the peaks for 124 aliphatic protons (protons of palmitate parts) at δ 0.880, 1.260, 1.620 and 2.500 (-CO-$\underline{CH_2}$-R). The peaks with meta coupling at δ 6.589 (d, 1H, J=2.13), 6.736 (d, 1H, J=2.13), 7.104 (d, 1H, J=2.13) represented for protons at 8,6 and 3′ position, that can not be specified the certain position. The peak of H-6′ that was ortho coupling with H-5′, appeared at δ 7.544 (d,1H, J=8.55). The peak at 7.135 (q, 1H, J=2.13; 2.13; 8.55) represented for H-5′, that was ortho coupling with

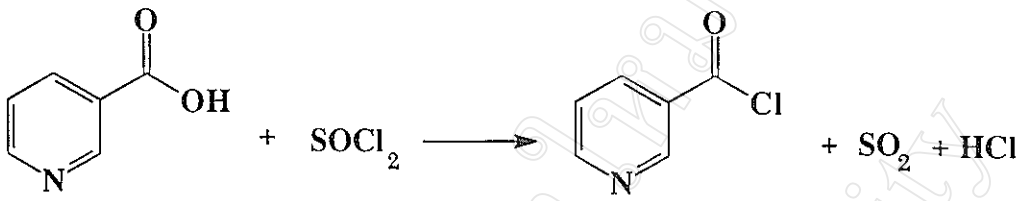
H-6′. The peak at δ 12.119 (s, 1H, OH) was proton of hydroxyl group at 5 position, that had hydrogen bond interaction with 4-carbonyl group.

The mass spectrum (see pages 91, 92) did not show molecular ion (M^+) peak at m/e = 1256 [calculated molecular weight of morin-3,5,7,2′,4′-tetrapalmitate = 1255.91], because the C-O bond of carboalkoxy groups at 3 and 2′-position easily broken down. The peaks at m/e 779, 514 and 302 represented for $M^+ - 2CO(CH_2)_{14}CH_3 + 2H^{\cdot}$, $M^+ - 3CO(CH_2)_{14}CH_3 + 3H^{\cdot}$ and $M^+ - 4CO(CH_2)_{14}CH_3 + 4H^{\cdot}$ fragment ions, respectively

MORIN-3,5,7,2′,4′-PENTANICOTINATE

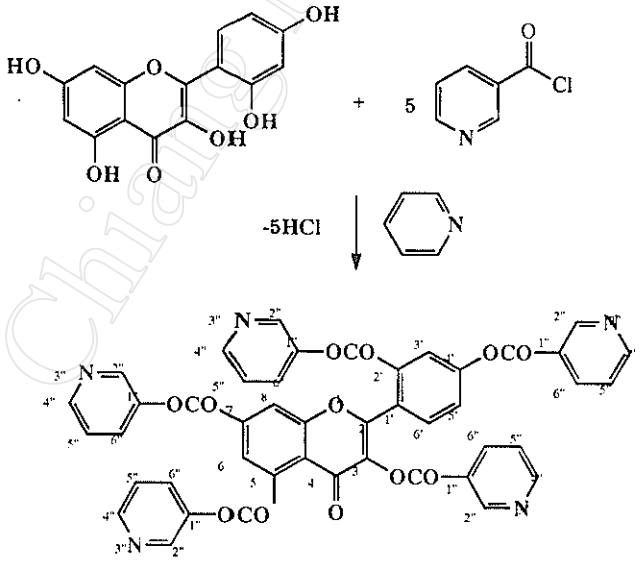
Morin-3,5,7,2′,4′-pentanicotinate was synthesized by two steps reaction.

First step, nicotinoyl chloride was synthesized from the reaction of nicotinic acid with thionyl chloride in pyridine solvent. Overall reaction is,



The mechanism of reaction is shown in figure 5.

Second step, morin-3,5,7,2′,4′-pentanicotinate was synthesized by esterification of morin with nicotinoyl chloride. Pyridine was used as solvent, and to react with hydrochloric acid generated in reaction. Overall Reaction is,



The mechanism of reaction is shown in figure 6.

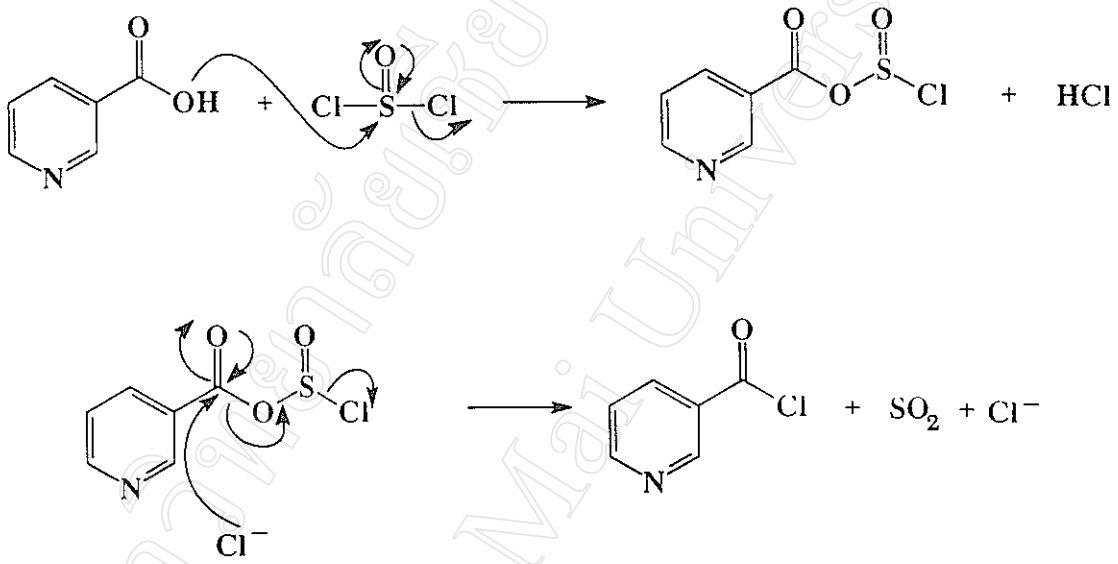


Figure 5 The mechanism of the formation of nicotinoyl chloride.

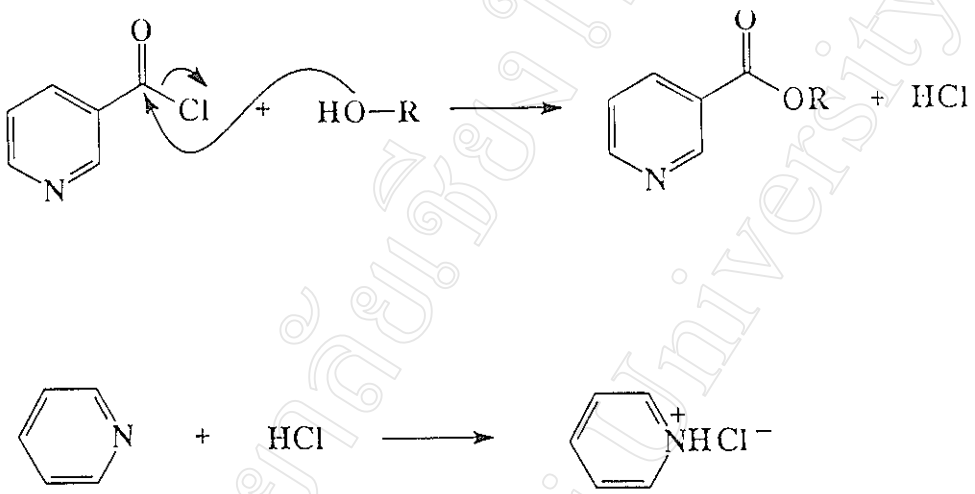


Figure 6 The mechanism of the formation of morin-3,5,7,2′,4′-pentanicotinate.

The structure of morin-3,5,7,2′,4′-pentanicotinate was confirmed by UV-Visible spectrum, IR spectrum, ^{1}H-NMR spectrum and mass spectrum.

The UV-Visible spectrum (see page 69) showed λmax at 300.47 nm and 254.42 nm that represented for aromatic chromophore.

The IR spectrum (see page 74) showed the peak of C=O harmonic vibration(overtone) at 3423.70 cm^{-1}. The strong peak at 1750.87 cm^{-1} represented for C=O stretching vibration of ester. The of C=O stretching vibration of cyclic conjugated ketone appeared at 1648.88 cm^{-1}.

The ^{1}H-NMR spectrum (see page 82-85) showed the peak of H-5′ that was ortho coupling with H-6′ and meta coupling with H-3′ at δ 7.384 (q, 1H, J=2.13; 2.13; 8.55). The peaks with meta coupling at δ 7.216 (d, 1H, J=2.13), 7.404 (d,1H, J=2.13) and 7.445 (d, 1H, J=2.13) assigned for protons at 8, 6 and 3′ position, that can not be specified the certain position. The peak of H-6′ that was ortho coupling with H-5′, appeared at δ 7.797 (d, 1H, J=8.55). The peaks at δ 7.490-7.554 (m, 5H) represented for five protons of nicotinate parts at 5″ position (H-5″) that were ortho coupling with H-4″ and H-6″. The peaks at δ 8.270

(m, 1H), 8.392 (m, 1H), 8.448 (m, 1H), 8.475 (m, 1H) and 8.546 (m, 1H) represented for five protons of nicotinate parts at $6^{//}$ position (H-$6^{//}$) that were ortho coupling with H-$5^{//}$ and meta coupling with H-$2^{//}$ and H-$4^{//}$. Five protons at $4^{//}$ position (H-$4^{//}$) of nicotinate parts appeared at δ 8.797 (q, 1H, J=1.83; 1.83; 4.88), 8.828 (q, 1H, J=1.83; 1.83; 4.88), 8.868 (q, 1H, J=1.83; 1.83; 4.88), 8.885 (q, 1H, J=1.83; 1.83; 4.88) and 8.922 (q, 1H, J=1.83; 1.83; 4.88). These protons were ortho coupling with H-$5^{//}$ and meta coupling with H-$6^{//}$, and tended to be meta coupling with H-$2^{//}$ which can be considered from the top of some peaks that quite broad. The peaks at δ 9.169 (d, 1H, J=1.83), 9.318 (d, 1H, J=1.83), 9.382 (d, 1H, J=1.83), 9.392 (d, 1H, J=1.83) and 9.405 (d, 1H, J=1.83) represented for protons at $2^{//}$ position (H-$2^{//}$) of nicotinate parts that were meta coupling with H-$6^{//}$. H-$2^{//}$ tented to be meta coupling with H-$4^{//}$ too, which can be considered from the top of peak that splitted to very small doublet.

The mass spectrum (see page 93) showed molecular ion (M^+) peak at m/e = 828 [calculated molecular weight of morin-3,5,7,$2^{/}$,$4^{/}$-pentanicotinate = 827.71]. The peaks at m/e 723, 618 and 513 represented for $M^+ - COC_5H_4N + H^{\cdot}$, $M^+ - 2COC_5H_4N + 2H^{\cdot}$ and $M^+ - 3COC_5H_4N + 3H^{\cdot}$ fragment ions, respectively.