

## STUDIES ON THE CONSTITUENTS OF *MURRAYA PANICULATA* JACK (I)

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The components of the flowers and fruits of *Murraya paniculata* (L.) Jack (Rutaceae) were examined. Scopolin, scopoletin and glucose from the former, and scopoletin and glucose from the latter were isolated and identified, respectively.

As the earlier phytochemical works of *Murraya paniculata* (L.) Jack (Rutaceae), Cadinene, the volatile oil component of leaves and barks, and murrayin, the glucoside component, which does not characterize of leaves and flowers, have been recorded in the book<sup>1)</sup>, and scopolin has been isolated from the petals<sup>2)</sup>. Recently, several coumarin components, coumurrayin, phebalosin, coumurrayin, osthol, and mexotcin, paniculatin and 3, 3', 4', 5, 5', 6, 7-heptamethoxy flavone have been identified from the ripe fruits<sup>3)</sup>, and leaves<sup>4-7)</sup> of this plant. In order to clarify the constituents of this species growing in Taiwan, the flowers and fruits were first examined. Consequently, scopolin (I), scopoletin (II) and glucose from the former, and scopoletin (II) and glucose from the latter were obtained, respectively.

Scopolin (I), the hydrolysed solution with 10% sulfuric acid reduced the Fehling's solution, was recrystallized from methanol as colorless needles with *mp.* 214°C,  $C_{16}H_{18}O_9 \cdot H_2O$ ,  $\lambda_{max}^{E_1OH}$  229, 292.5, 343  $m\mu$  ( $\log \epsilon$  4.27, 3.97, 4.04), and  $\nu_{max}^{KBr}$  3380-3470  $cm^{-1}$  (OH) and 1720  $cm^{-1}$  (CO).

Hydrolysis of scopolin (I) with 10% sulfuric acid afforded scopoletin (II), a colorless needle crystal with *mp.* 204°C which is identical (mixed *mp.* and IR (KBr)) with authentic scopoletin (II), and glucose, which osazone was identical (mixed *mp.*, IR (KBr), and T. L. C.) with authentic glucosazone.

Scopoletin (II) was recrystallized from acetone, as colorless needles with *mp.* 204°C,  $C_{10}H_8O_4$ ,  $\lambda_{max}^{E_1OH}$  229, 252.5, 298.5, 346.5  $m\mu$  ( $\log \epsilon$ , 4.23, 4.03, 3.98, 4.21) which revealed to 6, 7-disubstituted coumarin<sup>8)</sup> and  $\nu_{max}^{KBr}$  3340 (OH) and 1705 (CO)  $cm^{-1}$ , and NMR spectrum ( $C_2D_5N + CDCl_3$ ) exhibited a singlet of two aromatic protons at 3.15  $\tau$  and two doublet protons of A B type at 3.85 and 2.42  $\tau$  and a singlet of methoxy protons at 6.14  $\tau$ . It was identical (mixed *mp.*, IR (KBr), and T. L. C.) with authentic scopoletin (II).

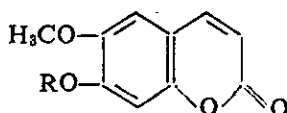
Glucose was obtained as osazone, and orangish yellow crystal with *mp.* 200-201°C and which

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was identical (mixed *mp.* IR (KBr), and T. L. C.) with authentic glucosazone.



(I) R=Glucosyl

(II) R=H

(III) R=COCH<sub>3</sub>

## EXPERIMENTAL

All melting points were uncorrected, IR spectra were recorded with Perkin-Elmer Infrared spectrophotometer. The NMR signals were obtained in  $\tau$  units using a JEOL-C-60 HL spectrophotometer with (CH<sub>3</sub>)<sub>4</sub>Si as internal standard. The UV spectra were measured on Shimadzu UV-200 double beam spectrophotometer.

### Extraction and Isolation

The fresh flowers (650 gm) of *Murraya paniculata* collected in Tainan, Taiwan, on August, 1973, were successively extracted with hot methanol for two times. The combined methanol extract was removed methanol under reduced pressure.

*Scopolin (I)*: The residue was put in refrigerator for twenty days to yield a colorless needle crystal (6.96 g, 1.07% in yield), recrystallized from methanol, *mp.* 214°C, UV  $\lambda_{\text{max}}^{\text{EtOH}}$   $\mu\mu$  (log  $\epsilon$ ): 229 (4.27), 292.5 (3.97), 343 (4.04), and IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 3380-3470 (broad, OH), 1720 (conjugated C=O). *Anal.* calcd. for C<sub>16</sub>H<sub>18</sub>O<sub>9</sub>·H<sub>2</sub>O: C, 51.61; H, 5.41. Found: C, 51.80; H, 5.10.

*Hydrolysis of scopolin (I)*: 200 mg of I was refluxed with 20 ml of 10% sulfuric acid and 30 ml of ethanol on the water bath for 7 hrs.

*Scopoletin (II)*: After removing ethanol under reduced pressure, the residue was extracted with ether. The ether solution was evaporated to leave scopoletin (II) (84 mg), a colorless needle crystal (from acetone), *mp.* 204°C which was identical (mixed *mp.*, IR, and T. L. C.) with authentic scopoletin (II).

*Glucose*: The aqueous solution free from scopoletin (II) was neutralized with BaCO<sub>3</sub> and condensed under reduced pressure. The concentrated solution which gave positive reaction to Fehling's solution and showed one spot which was the same R<sub>f</sub> value as D-glucose on T. L. C., was warmed on the water bath with sodium acetate and phenylhydrazine hydrochloride for 30 minutes to give osazone as orangish yellow needles, *mp.* 200-201°C, which was identical (mixed *mp.* and IR) with authentic glucosazone.

*Scopoletin (II)*: After separating scopolin (I), the dark brown mother liquor was extracted with ether. The ether solution was evaporated to leave a white crystal (5.2 g, 0.8% in yield), recrystallized from acetone, *mp.* 204°C. *Anal.* Calcd. for C<sub>10</sub>H<sub>8</sub>O<sub>4</sub>: C, 62.50; H, 4.20. Found: C, 62.57; H, 3.81 UV  $\lambda_{\text{max}}^{\text{EtOH}}$   $\mu\mu$  (log  $\epsilon$ ): 229 (4.23), 252.5 (4.03), 298.5 (3.98), 346.5 (4.21); IR  $\nu_{\text{max}}^{\text{KBr}}$   $\text{cm}^{-1}$ : 3340 (OH), 1705 (conjugated C=O); NMR (CDCl<sub>3</sub>+C<sub>3</sub>D<sub>3</sub>N)  $\tau$ : 6.14 (3H, S, C<sub>6</sub>-OCH<sub>3</sub>), 3.85 (1H, *d*, J=9Hz, C<sub>3</sub>-H), 3.15 (2H, S, C<sub>5</sub>, C<sub>6</sub>-H), 2.42 (1H, *d*, J=9Hz, C<sub>4</sub>-H).

It was identical (mixed *mp.*, IR. and T.L.C.) with authentic scopoletin (II).

*Acetylation of Scopoletin (II)*: Acetylation of II (200 mg). by acetic anhydride-pyridine yielded III as colorless needles (172 mg), *mp.* 184–185°C. *Anal.* calcd for  $C_{12}H_{10}O_5$ : C, 61.54; H, 4.30. Found: C, 61.13; H, 4.12. UV  $\lambda_{max}^{EtOH}$   $m\mu$  ( $\log \epsilon$ ): 223 (4.34), 275.5 (4.23), 334 (4.14). IR  $\nu_{max}^{KBr}$   $cm^{-1}$ : 1720 (conjugated C=O), 1752 (ester C=O). NMR ( $CDCl_3$ )  $\tau$ : 7.64 (3H, S,  $COCH_3$ ), 6.12 (3H, S,  $C_6-OCH_3$ ), 3.62 (1H, *d*,  $J=9Hz$ ,  $C_3-H$ ), 3.04 (1H, S,  $C_5-H$ ), 2.95 (1H, S,  $C_6-H$ ), 2.37 (1H, *d*,  $J=9Hz$ ,  $C_4-H$ ).

*Glucose*: The aqueous mother liquor which was shaken with ether was treated with sodium acetate and phenylhydrazine hydrochloride on the water bath for 30 minutes, to afford an orangish-yellow colored osazone (15.65 g, 2.1% in yield), *mp.* 200–201°C, which was identical (mixed *mp.*, IR., and T.L.C.) with authentic glucosazone which suggested glucose.

When the fresh fruits (600 gm) were treated by the same method as that of the flowers, scopoletin (II) (2.4 g, in yield 0.4%) and glucose (16.2 g, 2.7% in yield as osazone) were obtained.

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