

The whole dried plant (410 g) was extracted  $3 \times$  MeOH: after removal of the solvent *in vacuo*, the residue was extracted  $3 \times$  200 ml 1% HCl. The acidic fraction was basified with ammonia and extracted with  $\text{CHCl}_3$  giving 380 mg solid. Preparative TLC of this residue [ $\text{SiO}_2/\text{CHCl}_3$  with  $\text{Ce}^4(\text{SO}_4)_2$  as spray reagent] gave 50 mg of *N,N'*-di-*o*-tolylethylendiamine.

*N,N'*-*Dt*-*o*-tolylethylendiamine. Recrystallization from *n*-pentane gave m.p. 70–71.  $\lambda_{\text{max}}$  247 nm ( $\log \epsilon$  4.46), 291 (3.77); in EtOH,  $\nu_{\text{max}}$  3460, 3420, 1612, 1592  $\text{cm}^{-1}$  in  $\text{CHCl}_3$ . NMR ( $\text{CDCl}_3$ , TMS)  $\delta$ , 2.10 (s, 6 H, 2 Me-aryl), 3.46 (s, 4 H, N– $\text{CH}_2$ – $\text{CH}_2$ –N), 3.30 (broad band removed with  $\text{D}_2\text{O}$ , 2 NH), 6.64 (m, 4 H aromatic protons ortho or ortho and para to NH), 7.05 (m, 4 H aromatic protons meta to NH). The lack of equivalence of the 4 meta protons showed the probable structure. MS: *m/e* 240 ( $\text{M}^+$ , 30) (found 240,  $1632 \pm 0.0027$ ; calc. for  $\text{C}_{16}\text{H}_{20}\text{N}_2$ : 240, 1626) 121 (89), 120 (100), 118 (19), 106 (17), 91 (49), 79 (4), 78 (3), 77 (10), 65 (23).

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## TRITERPENOID SAPOPENINS OF *SCHIMA MERTENSIANA*

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**Key Word Index**—*Schima mertensiana*; Theaceae; oleanene-type sapogenins; primulagenin A; dihydropriverogenin A;  $\text{A}_1$ -barrigenol; barringtonenol C;  $\text{R}_1$ -barrigenol.

**Plant.** *Schima mertensiana* Koidz. (Theaceae); syn. *S. boninensis* Nakai. **Source.** The Bonin Islands, Japan. **Previous work.** On related species. *S. kankawaensis* Hay ( $\text{A}_1$ -barrigenol)[1] and *S. liukiuensis* Nakai ( $\text{A}_1$ -barrigenol,  $\text{R}_1$ -barrigenol)[2].

**Present work.** The MeOH extractive of the bark of *S. mertensiana* was partitioned between *n*-BuOH– $\text{H}_2\text{O}$ . The saponin mixture obtained from the *n*-BuOH soluble portion after ordinary working-up procedures was subjected to acid hydrolysis followed by treatment with alkali and silica-gel chromatography. Primulagenin A ( $3\beta,16\alpha,28$ -trihydroxy-olean-12-ene)[3], dihydropriverogenin A ( $3\beta,16\alpha,22\alpha,28$ -tetrahydroxy-olean-12-ene)[4],  $\text{A}_1$ -barrigenol ( $3\beta,15\alpha,16\alpha,22\alpha,28$ -pentahydroxy-olean-12-ene)[5], barringtonenol C ( $3\beta,16\alpha,21\beta,22\alpha,28$ -pentahydroxy-olean-12-ene)[6], and  $\text{R}_1$ -barrigenol ( $3\beta,15\alpha,16\alpha,21\beta,22\alpha,28$ -hexahydroxy-olean-12-ene)[5] were obtained in the respective yields of 2.2, 6.0, 35.8, 7.2 and 13.3% (from the total saponin mixture), and identified with the authentic specimens by direct comparison (m.p., IR, TLC). This is the first time that primulagenin A, dihydropriverogenin A and barringtonenol C have been isolated from *Schima* species.

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## REFERENCES

1. Nozoe, T. and Kinugasa, T. (1935) *Nippon Kagaku Kaishi* **56**, 883.
2. Takahashi, T., Miyazaki, M., Yasue, M., Imakura, H. and Honda, O. (1963) *Nippon Mokuzai Gakkaishi* **9**, 59.
3. Bischof, B. and Jeger, O. (1948) *Helv. Chim. Acta* **31**, 1760.
4. Yosioka, I., Nishimura, T., Matsuda, A. and Kitagawa, I. (1971) *Chem. Pharm. Bull. (Tokyo)* **19**, 1186.
5. (a) Errington, S. G., White, D. E. and Fuller, M. W. (1967) *Tetrahedron Letters* 1289; (b) Ito, S., Ogino, T., Sugiyama, H. and Kodama, M. (1967) *ibid.*, 2289.
6. Yosioka, I., Nishimura, T., Matsuda, A. and Kitagawa, I. (1970) *Chem. Pharm. Bull. (Tokyo)* **18**, 1610.