

The whole dried plant (410 g) was extracted $3 \times \text{MeOH}$: after removal of the solvent *in vacuo*, the residue was extracted $3 \times 200 \text{ ml } 1\% \text{ HCl}$. The acidic fraction was basified with ammonia and extracted with CHCl_3 giving 380 mg solid. Preparative TLC of this residue [$\text{SiO}_2/\text{CHCl}_3$ with $\text{Ce}^{IV}(\text{SO}_4)_2$ as spray reagent] gave 50 mg of *N-N'*-di-*o*-tolylethylenediamine.

N-N'-Di-*o*-tolylethylenediamine. Recrystallization from *n*-pentane gave m.p. 70–71°. λ_{max} 247 nm ($\log \epsilon$ 4.46), 291 (3.77); in EtOH. ν_{max} 3460, 3420, 1612, 1592 cm^{-1} in CHCl_3 . NMR (CDCl_3 , TMS) δ : 2.10 (s, 6 H, 2 Me-aryl), 3.46 (s, 4 H, N- CH_2 - CH_2 -N), 3.30 (broad band removed with D_2O , 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 (M^+ , 30) (found 240, 1632 ± 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).

N-N'-Di-*p*-tolylethylenediamine was also prepared [2] giving the following NMR data: 2.22, 3.30 (s, 4 H, N- CH_2 - CH_2 -N), 3.55 (s, removed with D_2O , 2 NH), 6.53 and 6.96 (m, 4 H, aromatic protons meta, equivalents, from NH).

Acknowledgement—We thank Dr. J. Borja (Madrid) for the collection and identification of the plant and Dr. A. G. Martinez (Universidad Complutense, Madrid) for the MS data.

REFERENCES

1. Tutin, T. G. (1968) *Flora Europae* (Tutin, T. G., Heywood, V. H., Burges, N. A., Moore, D. M., Valentine, D. H., Walters, S. M. and Webb, D. A. eds.) Vol. 2, pp. 343. Cambridge, University Press, Cambridge.
2. Mills, W. S. (1900) *J. Chem. Soc.* **77**, 1020; Schouten, A. E. (1937) *Rec. Trav. Chim. Pays-bas* **56**, 560.

Phytochemistry, 1975, Vol. 14, p. 314, Pergamon Press. Printed in England.

TRITERPENOID SAPOGENINS OF *SCHIMA MERTENSIANA*

ISAO KITAGAWA, AKIRA INADA, MARI UTSUNOMIYA and ITIRO YOSIOKA

Faculty of Pharmaceutical Sciences, Osaka University, Toneyama, Toyonaka, Osaka, Japan

(Received 28 April 1974)

Key Word Index—*Schima mertensiana*; Theaceae; oleanene-type sapogenols; primulagenin A; dihydropriverogenin A; A₁-barrigenol; barringtogenol C; R₁-barrigenol.

Plant. *Schima mertensiana* Koidz. (Theaceae); syn. *S. boninensis* Nakai. **Source.** The Bonin Islands, Japan. **Previous work.** On related species. *S. kankawaensis* Hay (A₁-barrigenol)[1] and *S. liukuensis* Nakai (A₁-barrigenol, R₁-barrigenol)[2].

Present work. The MeOH extractive of the bark of *S. mertensiana* was partitioned between *n*-BuOH- H_2O . 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], A₁-barrigenol ($3\beta, 15\alpha, 16\alpha, 22\alpha, 28$ -pentahydroxy-olean-12-ene)[5], barringtogenol C ($3\beta, 16\alpha, 21\beta, 22\alpha, 28$ -pentahydroxy-olean-12-ene)[6], and R₁-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 sapo-

genol mixture), and identified with the authentic specimens by direct comparison (m.m.p., IR, TLC). This is the first time that primulagenin A, dihydropriverogenin A and barringtogenol C have been isolated from *Schima* species.

Acknowledgement—The authors are grateful to Dr. H. Ishii, Faculty of Pharmaceutical Sciences, Chiba University, Chiba, Japan for the plant material.

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. Yosiooka, 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. Yosiooka, I., Nishimura, T., Matsuda, A. and Kitagawa, I. (1970) *Chem. Pharm. Bull. (Tokyo)* **18**, 1610.