Table I

Product	Yield (%)	mp (°C)	Formula	Analysis (%) Calcd. C	Calcd. H	Calcd. N	Found C	Found H	Found N
I	78	185	$C_{12}H_{14}O_2N_4$	58.52	5.73	22.75	58.41	5.69	22.83
II	95	316	$C_{16}H_{14}ON_4$	69.05	5.07	20.13	69.01	5.08	20.35
III	70	322	$C_{11}H_{12}ON_4$	61.09	5.59	25.91	60.99	5.48	26.02

1,3-Dimethylalloxazine (IV)——A mixture of I (0.5 g, 0.002 mole) and sulfur (0.26 g, 0.008 g atom) was heated at 240—250° for 40 min under occasional stirring. Treatment of the tarry brown product with EtOH turned into powder, which was extracted with $(C_2H_5)_2O$ several times. The extracts gave upon evaporation a yellow powder (IV) (0.28 g, 58%), mp 241°, which was identified by infrared (IR) spectra.

4-Hydroxy-2-phenylbenzo[*g*]pteridine (V)——A mixture of II (0.10 g, 0.00036 mole) and sulfur (0.05 g, 0.0016 g atom) was heated at 240—250° for 20 min under occasional stirring. The crude product was recrystallized from EtOAc to afford a yellow powder (V) (0.08 g, 80%), mp >300°, which was identified with the authentic sample[4] in all respects.

4-Hydroxy-2-methylbenzo[*g*]pteridine (VI)——A mixture of III (0.12 g, 0.00056 mole) and sulfur (0.04 g, 0.0013 g atom) was heated at 250—260° for 40 min. The tarry product was washed with $(CH_3)_2CO$ to give the crude product as a brown powder. Recrystallization from EtOH gave VI as dark yellow powder (0.05 g, 42.4%), mp >300°. *Anal.* Calcd. for $C_{11}H_8ON_4$: C, 62.25; H, 3.80; N, 26.40. Found: C, 62.34; H, 3.91; N, 25.99.

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Constituents of Three Thai Medicinal Plants: *Ardisia polycephala* (Myrsinaceae), *Rhabdia lycioides* (Boraginaceae), and *Balanophora polyandra* (Balanophoraceae)[1]

Verapong Podimuang,[2] Stang Mongkolsuk,[3a] Kunitoshi Yoshihira, and Shinsaku Natori[3b]

Faculty of Medical Sciences, University of Medical Sciences, Bangkok[3a] and National Institute of Hygienic Sciences[3b]

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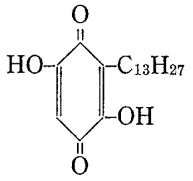
The root of *Ardisia polycephala* Wight (Myrsinaceae) (in Thai, Phi-Lang-Ka-Sa) is one of the shrubs used by Thai old style doctors as antivenom. An orange pigment was isolated from the hexane extract of the root in a high yield (1.4%) and identified with rapanone (I), one of the 2,5-dihydroxy-3-alkylbenzoquinone derivatives widely distributed among Myrsinaceae plants.[4,5]

The wood of *Rhabdia lycioides* Mart. (Boraginaceae) (in Thai, Takrai-Hangnak) is used as diuretic. The ether extract of the wood afforded a mixture of triterpenoids, from which

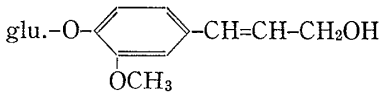
1) This paper constitutes Part V of "Studies on Thai Medicinal Plants" by S. Natori and K. Nishimoto. Part IV: K. Yoshihira, S. Natori, and P. Kanchanapee, *Tetrahedron Letters*, **1967**, 4857.
2) A part of this work was carried out at National Institute of Hygienic Sciences, where one of us (V. P.) stayed in 1969—1970 as a Columbo Plan Fellow.
3) Location: *a*) *Rama VI Road, Bangkok, Thailand*; *b*) *Kamiyoga-1-chome, Setagaya-ku, Tokyo.*
4) H. Ogawa and S. Natori, *Phytochem.*, **7**, 773 (1968).
5) R. Hegnauer, "Chemotaxonomie der Pflanzen," Band 5, Birkhäuser Verlag, Basel, 1969, p. 154.

bauerenol[6] was isolated as the acetate and identified. Since the Indian chemists reported, while our work was in progress, the presence of bauerenol, α-amyrin, and β-amyrin in the plant,[7] further characterization was abandoned.

The whole plant of *Balanophora polyandra* Griff. (Balanophoraceae) (in Thai, Hora-Teenmar) was claimed by the old style Thai doctors as antiasmatic. The plant material was successively extracted with petroleum ether, ether, and methanol. From petroleum ether and ether fractions β-amyrin acetate was isolated in 0.3% yield and identified. From methanol extract a glucoside of mp 186° was obtained in a high yield (0.72%). Physical properties of the compound and the acetate indicated that the compound might be coniferin (II) and the identity was confirmed by the comparison with the authentic sample. Coniferin is widely distributed among conifers and other plants and was once used in cough syrups. The use of the decoction of the herb as antiasmatic in Thailand has now been supported by the presence of coniferin in the plant.



I



II

Experimental

Isolation of Rapanone from the Roots of *Ardisia polycephala*——The dried roots (1.0 kg) was extracted with petroleum ether (bp 57—70°) in a Soxhlet apparatus for 48 hr and the combined extract was evaporated. The orange–red residue was recrystallized from ether to orange plates (14 g) of mp 138°. The identity with rapanone was confirmed by a mixed fusion, IR, and TLC. The alkaline hydrogen peroxide oxidation, followed by the examination using gas chromatography[4] of the methyl ester of the acid formed, revealed the compound is not contaminated with the homolog.

Isolation of Bauerenol from the Wood of *Rhabdia lycioides*——The dried heatwood (1.0 kg) was extracted with ether in a Soxhlet apparatus for 48 hr and the extract was recrystallized from ether–methanol to colorless plates (3.0 g) of mp 220°, which showed the presence of three triterpenoids by TLC and GLC. Acetylation of the mixture and recrystallization from chloroform–acetone afforded colorless needles of mp 282—284°, showing a single spot in TLC and GLC. The identity with bauerenyl acetate was confirmed by the comparison with the authentic sample. The mother liquor showed the presence of the acetates of α-amyrin and β-amyrin by TLC and GLC.

Isolation of β-Amyrin Acetate and Coniferin from *Balanophora polyandra*——The plant material was collected in the jungle of Nakornrachasima Province (north east of Bangkok). The whole dried plant (2.0 kg) was chopped into small pieces and extracted in a Soxhlet apparatus successively with petroleum ether (bp 50—70°) for 48 hr, with ether for 48 hr, and with methanol for 3 days. The each extracts were evaporated under reduced pressure. The petroleum ether extract was purified by passing through a column of alumina and colorless residue thus obtained was recrystallized from ether–methanol to colorless plates of mp 237—238°. Hydrolysis with KOH gave colorless needles (3.8 g) of mp 192—194°. Comparison with the authentic samples showed the compound is identical with β-amyrin acetate. The ether extract was purified by the same way and gave β-amyrin acetate (1.8 g).

The methanol extract was purified by recrystallization from dilute MeOH to give colorless plates (14.4 g) of mp 186°. IR ν_{max}^{Nujol} cm^{-1}: 3400—3300, 1592, 1518, 1080, 1048, 1028. NMR (in D_2O) δ: 3.52 (3H, s), 3.8 (4H), 4.17 (1H), 4.24 (1H), 4.9 (1H), 6.0—6.5 (2H), 6.9—7.2 (3H). Acetylation with $(CH_3CO)_2O$ gave an acetate of mp 130—132°. IR ν_{max}^{Nujol} cm^{-1}: 1760, 1735, 1240, 1045. NMR (in $CDCl_3$) δ: 1.99 (s, 6H), 2.03 (s, 9H), 3.75 (s, 3H), 4.1 (2H), 4.6 (1H), 4.7 (1H), 4.8—5.3 (4H), 5.8—6.4 (2H), 6.7—7.0 (3H). The comparison with the authentic samples of coniferin and the acetate showed the identity.

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7) P. Saradamma and A.S. Rao, *Current Science* (India), **38**, 89 (1969).