14. Masao Tomita, Yasuo Inubushi, and Noboru Mizoguchi: Studies on the Alkaloids of Berberidaceous Plants. V.[1] Alkaloids of *Mahonia japonica* DC. (2).

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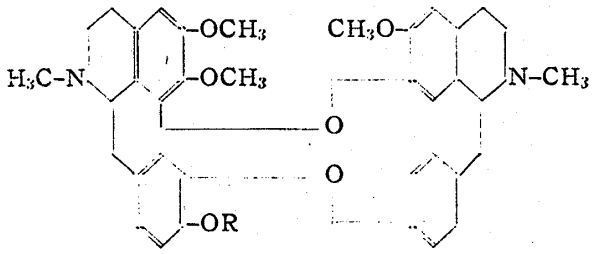
A study was previously made of the alkaloids of the trunk and root of *Mahonia japonica* DC., belonging to the genus Mahonia, which grows in Japan, by Tomita and Abe[1,2], who clarified that they both contain isotetrandrine and berbamine as tertiary bases, and jatrorrhizine, berberine, and palmatine as quaternary bases. This time, authors examined the alkaloids contained in the fruit of *Mahonia japonica* DC. and the results obtained are reported herein.

The fresh fruits collected in July, 1952, in the suburbs of Kyoto City were used as the material. From the parts of the pericarp and flesh, only a small amount of isotetrandrine was obtained, and no other base was detected, and from the part of the seed, isotetrandrine and berbamine were proved as tertiary bases as from the trunk and root of this plant, but no quaternary base was identified. The content of both bases in the seed is larger than in the trunk and root, and a comparison of their percentages is given in Table I.

TABLE I

	Percentage of alkaloids in alcohol extract	
	Trunk[1]	Seed
Isotetrandrine	0.890	2.333
Berbamine	0.007	0.666



R = CH_3 Isotetrandrine

R = H Berbamine

It was also found that the bases in the fruit are mostly contained in the seed, and only a small amount in the pericarp and flesh.

Experimental

Immediately after having been collected, the fruit of *Mahonia japonica* DC. was separated into pericarp and seed. The seed was air-dried, drained, and provided for the experiment.

Alkaloids of the seed—650 g. of the air-dried seed was drained and freed from fat by means of ether. The ether maceration was treated with 3% hydrochloric acid solution, to which the basic substance was transferred, and the hydrochloric acid solution was combined to that from the alcoholic extract. The seed freed from fat was extracted several times with warm methanol, and the methanol removed under reduced pressure, leaving 90 g. of a brown viscous residue. This residue was extracted several times with 3% hydrochloric acid, and filtered. The hydrochloric acid extracts were combined, washed with ether, and after being rendered alkaline with ammonia, extracted several times with ether followed by a few portions of chloroform. The ether and the chloroform extracts were respectively shaken with 3% aqueous sodium hydroxide solution to separate the phenolic base. The ether and the chloroform solutions were dried over anhydrous potassium carbonate, and the solvents removed. From the ether solution, colorless crystals soon deposited, and the residue from the chloroform solution crystallized on the addition of a small

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1) Part IV: M. Tomita, T. Abe: J. Pharm. Soc. Japan, 72, 773 (1952).

2) M. Tomita, T. Abe: J. Pharm. Soc. Japan, 72, 735 (1952).

portion of ether. The yield of the crude nonphenolic base was 2.1 g. The above crystals were both respectively recrystallized from acetone to colorless prisms, m.p. 180~181°, alone or mixed with a sample of isotetrandrine. *Anal.* Calcd. for $C_{38}H_{42}O_6N_2$: C, 73.27; H, 6.74. Found: C, 73.16; H, 6.79.

The above caustic alkali solution containing the phenolic base was neutralized once with hydrochloric acid, and then after alkalization with ammonia, extracted with ether. The ether solution was dried over anhydrous potassium carbonate, and the solvent distilled off, leaving an oily substance. When this was moistened with a small portion of benzene and kept overnight, needle-shaped crystals appeared. The yield was 0.59 g. Recrystallization from a small amount of benzene yielded colorless needles, m.p. 124~126°, undepressed by admixture with a sample of berbamine-benzene adduct. *Anal.* Calcd. for $C_{37}H_{40}O_6N_2 \cdot C_6H_6$: C, 75.22; H, 6.70. Found: C 75.39; H, 6.26.

The ammonia alkaline solution separated from the tertiary bases was acidified with acetic acid, and concentrated under reduced pressure. Addition of potassium iodide to this solution gave no precipitate, and no clouding occurred with the alkaloid reagent.

Alkaloids of the pericarp and flesh — Juice was pressed from the fruit, and the pericarp was extracted several times with warm methanol. The methanol was removed under reduced pressure, and the residue was extracted with 3% hydrochloric acid. This extract was combined with the fruit juice, filtered, and the filtrate was treated with basic lead acetate. The resulting precipitate was filtered, and the filtrate was freed from excessive lead salts by a passage of hydrogen sulfide. Then the solution was shaken with ether to remove ether-soluble impurities, and after being rendered alkaline with sodium bicarbonate, extracted with benzene. The extract was dried with anhydrous potassium carbonate, and the solvent evaporated by distillation, yielding 0.41 g. of a crude base. Addition of a small amount of ether to the crude base gave colorless crystals, m.p. 175~177°, which were recrystallized from acetone and showed m.p. 180°, either alone or on admixture with a sample of isotetrandrine. In the aqueous solution left after separation of the tertiary bases, no detectable amount of basic substance was recognized.

Summary

The authors examined the alkaloids of the fruits of *Mahonia japonica* DC., and proved the presence of isotetrandrine and berbamine, as previously obtained from its trunk and root by Tomita and Abe. It was found that the content of both bases in the plant is larger than in the trunk and root, and no quaternary bases, such as berberine, are contained in this part of the plant. It was also found that the bases of the fruit are largely contained in the seed, and are contained in a small amount in the pericarp and flesh.

(Received November 21, 1952)