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Tatsuo Kariyone, Yohei Hashimoto, and Seisho Tobinaga : Studies on Triterpenoids. IX.* The Chemical Constituent of Bird Lime extracted from *Rhododendron linearifolium* SIEB. ET ZUCC. VAR. *macrosepalum* MAKINO.**

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From the buds of *Rhododendron linearifolium* SIEB. ET ZUCC. VAR. *macrosepalum* MAKINO, a Japanese wild tree (mochitsutsuji), a viscous substance like bird lime was separated, which yielded ursolic acid, two kinds of new triterpenoid, and other components by saponification. The yield of greyish white lime amounted to 4.7% of buds of this plant by extraction with carbon tetrachloride. The chemical constants of lime of this plant and limes from several Japanese plant materials, including some market products, are indicated in Table I.

TABLE I.

Kind of bird lime	Acid value	Ester value[a)]	Source
Mochitsutsuji lime (buds)	10.4	19.3	Present author
Yadorigi lime (*Viscus album*)	12.0	119.6	Obata[1)]
White lime (*Ilex integra*?)	26.6	86.6	Yanagisawa[2)]
Red lime (*Trochodendron aralioides*?)	21.8	105.8	〃

a) The measurement carried out by boiling with *N* ethanolic KOH during 3 hrs.

The yellowish resinous matter from ethanol extract of this plant bud was saponified by boiling with 30% ethanolic KOH for 50 hours, calcium chloride added, and extracted with carbon tetrachloride to separate the unsaponifiable matter.

Ursolic acid, m.p. 289°; melissyl alcohol m.p. 85°; a triterpenoid alcohol, m.p. 217°, $[\alpha]_D^{24}$ −27.4°; $C_{30}H_{50}O$(acetate), m.p. 256°, $[\alpha]_D^{24}$ −11.7°; and a carboxylic acid, m.p. 283°, $C_{30}H_{48}O_3$, were separated from the unsaponifiable matter. It is assumed that ursolic acid is partially conjugated with fatty acid as well as other alcohols in the lime, since it has a hydroxyl group. The terpene alcohol was not identical with any compound reported hitherto, although further examinations were made, comparing also with ilexsol by Iseda.[3)] The triterpene-carboxylic acid was regarded as an isomer of oleanolic acid, ursolic acid, or the like, but it showed a marked depression of the melting point when mixed with these isomeric compounds. This new triterpene alcohol and acid were designated as motiol and motic acid, respectatively, although the very small amount available has not permitted further detailed study.

Experimental

Extraction and Saponifications of Lime Constituents—1.6 kg. of pale grey viscous matter was extracted from 34 kg. of buds of "Mochitsutsuji" by CCl_4, saponified with 30% EtOH-KOH for 50 hrs., the saponified product was poured into $CaCl_2$ solution, and mixed throughly. The precipitate was filtered by suction and then extracted with CCl_4 Insoluble part was acidified with HCl to form oily fatty acid layer which was refined and dried by dissolving in CCl_4. Its neutralization value (195.0) and iodine value (20.0) were measured. On acidification, a flocculent precipitate formed in the boundary between CCl_4 and HCl layer, which was collected on a filter and boiled, together

* Part Ⅷ. T. Kariyone, S. Ishimasa, T. Shiomi : J. Pharm. Soc. Japan, **76**, 1210(1956).

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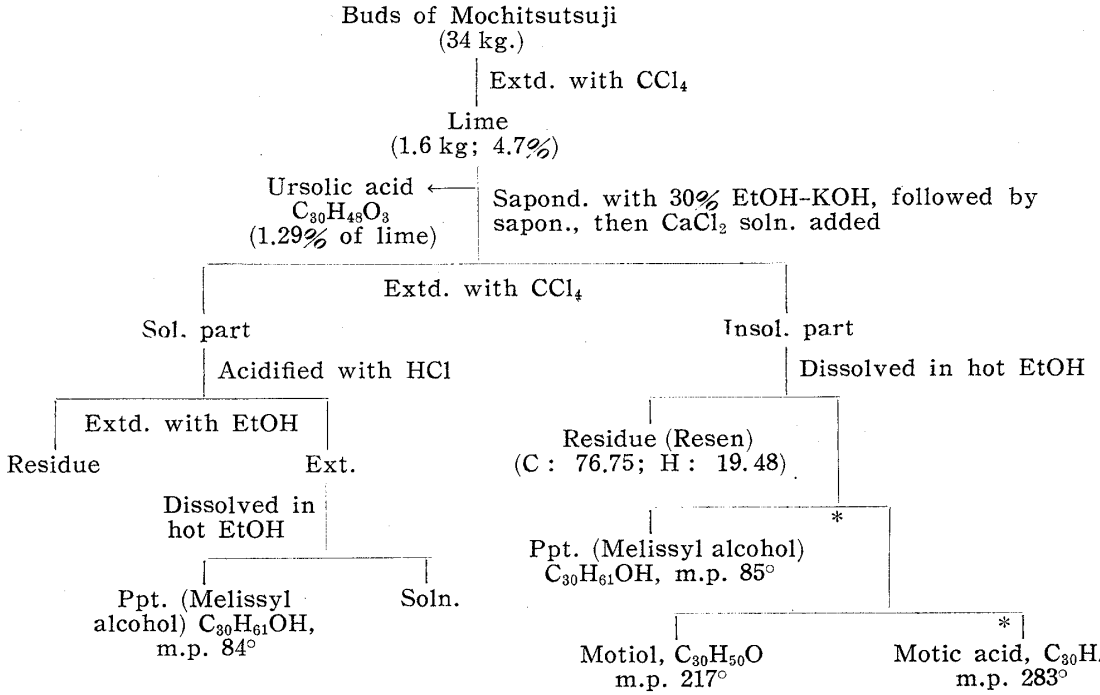
1) Y. Obata : J. Agr. Chem. Soc. Japan, **17**, 222, 784(1945).
2) H. Yanagisawa : J. Pharm. Soc. Japan, **41**, 495(1921).
3) S. Iseda : J. Pharm. Soc. Japan, **72**, 1064, 1611(1952).

with the filter paper, with hot 10% KOH solution, and the extraction was repeated. The total extract was acidified with HCl, the precipitate formed was dissolved in alkali by boiling, and reprecipitated with HCl. Reprecipitation was repeated in this way, and finally a fairly white amorphous fraction of ursolic acid that separated was repeatedly recrystallized from EtOH to ursolic acid as pure white needles, m.p. 289°(corr.), identical with an authentic sample. From CCl_4 layer, motiol, motic acid, and melissyl alcohol were separated by recrystallization and purification, which are shown in Chart 1.



* From the EtOH solution of motic acid—motiol mixture, a flocculent precipitate of motic acid was separated by shaking with 10% KOH solution in a separatory funnel.

Chart 1.

Motiol—Purified from EtOH to pure white needles, m.p. 217°(corr.); $[\alpha]_D^{24}$ −27.4°(in $CHCl_3$). *Anal.* Calcd. for $C_{30}H_{50}O$: C, 84.44; H, 11.81. Found : C, 84.34; H, 11.24.

Motiol Acetate—Motiol was boiled for 1 hr. with Ac_2O and recrystallized from EtOH; m.p. 256° (corr.); $[\alpha]_D^{24}$ −11.7°(c=0.425, in $CHCl_3$). *Anal.* Calcd. for $C_{32}H_{52}O_2$: C, 81.99; H, 11.18. Found : C, 81.56; H, 10.88.

Motic Acid—Precipitated K salt of motic acid was separated and repeatedly recrystallized from EtOH to pure motic acid, m.p. 283~284°(corr.); $[\alpha]_D^{12}$ −73.40 (c=0.865, in $CHCl_3$). *Anal.* Calcd. for $C_{30}H_{48}O_3$: C, 78.89; H, 10.59. Found C, 78.78; H, 10.21.

A marked depression of m.p. was observed on admixture with authentic samples of oleanolic acid and ursolic acid.

Liebermann-Burchard reaction gives a continuous violet red color, and a pale yellow color with tetranitromethane revealed the presence of a double bond. Tschugaeff's reaction[4] was violet red.

Motic Acid Acetate—Readily prepared by the usual acetylation process; m.p. 191~192°(corr.). *Anal.* Calcd. for $C_{32}H_{52}O_4$: C, 76.75; H, 10.47. Found C, 76.33; H, 10.06.

Summary

By the extraction of buds of *Rhododendron linearifolium* SIEB. ET ZUCC. VAR. *macrosepalum* MAKINO, a presence of a viscous matter was discovered, the properties of which were very similar to those of bird lime in Japanese market. By its saponification, ursolic acid, melissyl alcohol, motiol, and motic acid were separated. The latter two were proved to be new triterpenoids with following constants : Motiol, $C_{30}H_{50}O$, m.p. 217°, $[\alpha]_D^{24}$ −27.4. Motic acid, $C_{30}H_{50}O_3$, m.p. 283~284°, $[\alpha]_D^{12}$ −73.40.

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4) T. Kariyone, Y. Hashimoto : J. Pharm. Soc. Japan, **70**, 50(1950).