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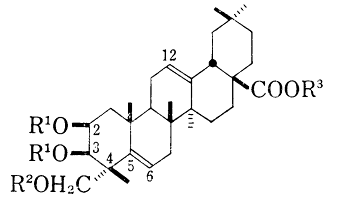
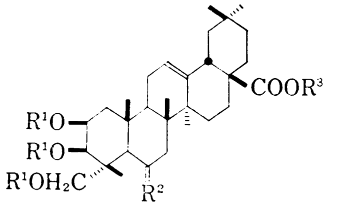
Protobassic Acid, a Genuine Sapogenol of Seed Kernels of *Madhuca longifolia* L.

Bassic acid(Ia) has been characterized as a sapogenol commonly occurring among several *Sapotaceous* plants.[1,2] The chemical constitution of bassic acid was initially proposed by Heywood and Kon[1] and was later established by King and Yardley[3] as Ia, which is significant by the possession of an additional double bond at C-5 in the olean-12-ene skeleton.

During the course of the study on the chemical constitution of saponin isolated from the seed kernels of *Madhuca longifolia* L. (Sapotaceae), we have noticed by virtue of the soil bacterial hydrolysis method[4] that bassic acid is an artifact sapogenol whereas a new compound now named protobassic acid(IIa) is a genuine one. The present communication deals



Ia : $R^1=R^2=H$, $R^3=H$
(bassic acid)
Ib : $R^1=R^2=H$, $R^3=CH_3$
Ic : $R^1=R^2=Ac$, $R^3=CH_3$
Id : $R^1=(CH_3)_2C<$, $R^2=H$, $R^3=CH_3$



IIa : $R^1=H$, $R^2=\beta OH$, αH, $R^3=H$
(protobassic acid)
IIb : $R^1=H$, $R^2=\beta OH$, αH, $R^3=CH_3$
IIc : $R^1=Ac$, $R^2=\beta OH$, αH, $R^3=CH_3$
IId : $R^1=Ac$, $R^2=O$, $R^3=CH_3$

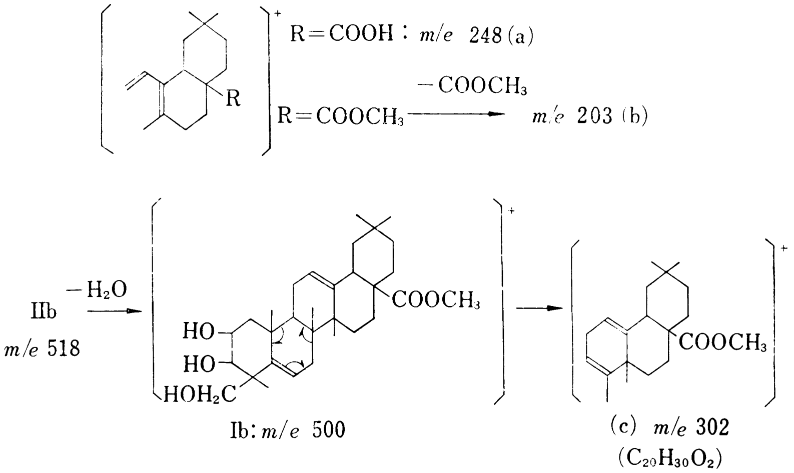


Chart 1

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1) B.J. Heywood and G.A.R. Kon, *J. Chem. Soc.*, **1940**, 713.

2) J. Simonsen and W.C.J. Ross, "The Terpenes," Vol. V, Cambridge, at the University Press, 1957, pp, 139—147.

3) T.J. King and J.P. Yardley, *J. Chem. Soc.*, **1961**, 4308.

4) *a*) I. Yosioka, M. Fujio, M. Osamura, and I. Kitagawa, *Tetrahedron Letters*, **1966**, 6303; *b*) I. Yosioka, K. Imai, and I. Kitagawa, *Tetrahedron Letters*, **1967**, 2577; *c*) I. Yosioka, T. Sugawara, A. Ohsuka, and I. Kitagawa, *Chem. Pharm. Bull.* (Tokyo), **19**, 1700 (1971); *d*) I. Yosioka, K. Imai, and I. Kitagawa, *Tetrahedron Letters*, **1971**, 1177.

with the preliminary account on protobassic acid leading to the structure IIa.

On acid hydrolysis followed by silica gel column chromatography, the saponin mixture obtainable in 10% yield from the above mentioned seed kernels collected at Jaffna in Ceylon after the ordinary procedure afforded majorly bassic acid(Ia),[5] $C_{30}H_{46}O_5$,[6] mp 289—291°, $[\alpha]_D+87.5°$(pyridine), IR ν_{max}^{KBr} cm^{-1}: 3430(br.)(OH), 1689(COOH); methyl ester(Ib), $C_{31}H_{48}O_5$, mp 218—219°, $[\alpha]_D+55°$($CHCl_3$), IR ν_{max}^{KBr} cm^{-1}: 3425(OH), 1710, 1725($COOCH_3$); methyl ester triacetate(Ic), $C_{37}H_{54}O_8$, mp 146—148°, $[\alpha]_D+69.6°$($CHCl_3$), IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1743, 1236 (br.)($OCOCH_3$, $COOCH_3$); methyl ester monoacetonide(Id), $C_{34}H_{52}O_5$, mp 209—210°, $[\alpha]_D$ $+65.7°$($CHCl_3$), IR ν_{max}^{KBr} cm^{-1}: 3505(OH), 1710($COOCH_3$)(in lit.[1] Ia: mp 316°, $[\alpha]_D+82.9°$ (pyridine); Ib: mp 216—217°, $[\alpha]_D+56.2°$($CHCl_3$); Ic: mp 148—149°; Id: mp 205—206°).

On the other hand, the soil bacterial hydrolysis[7] applied on the same saponin mixture as presented before[4] (cultivated at 33° for 27 days) furnished a new compound as a sole sapogenol which is unidentical with bassic acid and is designated as protobassic acid. It is noteworthy to mention that there has been no indication of bassic acid among the total hydrolysate.

TABLE I. The PMR Data obtained in $CDCl_3$ (in τ Values)[a]

	Ic[b]	IIc[c]
$-\overset{\vert}{\underset{\vert}{C}}-C\underline{H}_3$	9.06 (6H), 9.05, 8.95, 8.74, 8.64 (3H, each) (all s)	9.08 (sh), 9.04 (totally 6H), 8.93, 8.89, 8.56, 8.39 (3H, each) (all s)
$-OCOC\underline{H}_3$	8.01, 7.96, 7.92 (3H, each, s)	7.99, 7.96, 7.93 (3H, each, s)
$-COOC\underline{H}_3$	6.37 (3H, s)	6.36 (3H, s)
$-C_{(23)}\underline{H}_2OAc$	5.78, 6.19 (2H, ABq, $J=12$ Hz)	6.09 (2H, br.s, $W_{h/2}=3.2$ Hz)
$\rangle C_{(6)}\underline{H}-\beta OH$	——	5.55 (1H, m, $W_{h/2}=8$ Hz)
$=C_{(6)}\underline{H}-$	4.30—4.50 (1H, m)	——
$\rangle C_{(3)}\underline{H}-\beta OAc$	4.98 (1H, d, $J=4$ Hz)	5.11 (1H, d, $J=4$ Hz)
$\rangle C_{(2)}\underline{H}-\beta OAc$ $=C_{(12)}\underline{H}-$	4.52—4.68 (2H)[d]	4.48—4.75 (2H)[d]

a) abbreviation: ABq=AB type quartet, br.s=broad singlet, d=doublet, m=multiplet, s=singlet
b) measured at 100 MHz.
c) measured at 60 MHz.
d) Signal patterns are unclear due to the overlapping.

Protobassic acid(IIa), $C_{30}H_{48}O_6$, mp 310—312°, $[\alpha]_D+22.7°$(pyridine), IR ν_{max}^{Nujol} cm^{-1}: 3550, 3450(OH), 1675(COOH), gave a methyl ester(IIb), $C_{31}H_{50}O_6 \cdot 1/2 H_2O$, mp 198—201°, $[\alpha]_D+42.4°$(MeOH), IR ν_{max}^{KBr} cm^{-1}: 3400(br.)(OH), 1725($COOCH_3$), with ethereal diazomethane, and the methyl ester in turn furnished with acetic anhydride and pyridine at room temperature a methyl ester triacetate(IIc)(amorphous), $C_{37}H_{56}O_9$, IR ν_{max}^{Nujol} cm^{-1}: 3540(OH), 1755, 1247(br.)($OCOCH_3$, $COOCH_3$), in which one hydroxyl function was left unattacked.

On treatment with phosphorus oxychloride in pyridine followed by the alkaline hydrolysis, IIc afforded Ib as a single product, whereas CrO_3-pyridine oxidation of IIc yielded a carbonyl compound(IId), $C_{37}H_{54}O_9$, mp 164—167°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1745(br.)($OCOCH_3$, $COOCH_3$), 1715(CO), whose carbonyl function was revealed to resist against ordinary Huang-Minlon reduction. Furthermore, acid treatment of IIb under the similar condition as for hydrolysis of saponin yielded Ib as a major product along with some other secondary products.

The mass spectra of IIa and IIb (base peaks at *m/e* 248(a) and 203(b)) are in close resemblance to those of Ia and Ib (base peaks: (a) and (b)) respectively except that the molecular ions of the former pair are observed at *m/e* 504(IIa) and 518(IIb) of 18 mass unit more than

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[5] Although the direct comparison with authentic bassic acid has been unavailable, the accumulated evidences for the sapogenol presented here clearly assure its identity with bassic acid.
[6] All the compounds given with the chemical formulae gave the satisfactory analytical values.
[7] The soil bacterial strain YSB-15, unidentified yet, was used.

those of the latter pair. The spectra also exhibit the ion peaks due to dehydration at m/e 486(in IIa) and m/e 500(in IIb) being coincided with the molecular ions of Ia and Ib. Especially of significance is that a fragment peak at m/e 302(c)[8] due to the reverse Diels-Alder type fragmentation in ring B of Ib is also observed in the mass spectrum of IIb, which suggests that a hydroxyl function in IIb locates at C-5 or C-6 and is readily dehydrated furnishing a double bond at C-5.

The C-6β-OH(axial) is preferred for IIa as based on the chemical property of IIa for acetylation and that of the derived carbonyl function in IId along with the proton magnetic resonance (PMR) assignment as given in Table I. A one-proton multiplet at 5.55 τ ($W_{h/2}$= 8 Hz) of IIc is assignable to C-6α-H (equatorial).[9] Three C-methyl functions among six C-methyls (all observed as singlets) probably at C-4β, C-10β, and C-8β are observed paramagnetically shifted by suffering the anisotropic effect of C-6-OH, which is therefore considered to possess β-axial configuration.

Consequently, the structure IIa is proposed for protobassic acid. It is interestingly presumed that protobassic acid may be a genuine sapogenol of several *Sapotaceous* plants, in which bassic acid had been recognized as the common sapogenol. The structure of saponin is now under investigation.

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[8] Comfirmed by the high resolution mass spectrometry. Very recently, the ion(c) has also been described as a fragment ion of methyl sumaresinolate and its 6-oxo derivative by I. Wahlberg and C.R. Enzell (*Acta Chem. Scand.*, **25**, 70 (1971)).

[9] N.S. Bhacca and D.H. Williams, "Applications of NMR Spectroscopy in Organic Chemistry," Holden-Day, Inc., San Francisco, 1964, p. 79.

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Thermal Hydrogen-Deuterium Exchange Reaction between Aromatic Ring Deuterium and Active Hydrogen of Substituent Group

With regard to the hydrogen-deuterium exchange reactions of organic compounds, numerous papers[1a-d] were presented. This communication is concerned to the thermal hydrogen-deuterium exchange observed in the substituted aromatics with active hydrogen atom on the substituent group. We prepared the deutrium labelled compounds by ordinary methods from

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