

A New Triterpene, Phytolaccagenic Acid from *Phytolacca americana*

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商陸의 新成分 Phytolaccagenic Acid 에 관한 연구

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商陸(*Phytolacca americana* L.)의 根에서 얻은 粗 saponin 을 酸 加水分解하면 5種의 genin을 얻을 수 있다. 그 中 2種의 成分에 대하여는 아직 그 構造가 밝혀지지 않았다. 그 中 한 成分 $C_{31}H_{48}O_6$, (mp 309—311°)에 대하여 理化學的 性質을 檢討한 바 I과 같은 構造式을 推定할 수 있었으며 本成分은 新化合物이므로 phytolaccagenic acid 라고 命名하였다.

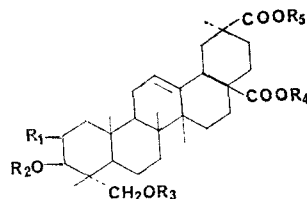
Phytolaccagenic acid 의 加水分解產物은 第 2의 未知成分과 같고 이것은 *P. esculenta* 에서 얻은 esculentic acid 와 同一하다.

In 1949, AHMED, ZUFALL, and JENKINS¹⁾ reported the isolation of the toxic principle from poke weed (*Phytolacca americana* L.) having the molecular formula $C_{55}H_{90}O_{22} \cdot 2H_2O$ and its biological actions. In 1964, STOUT, MALOFSKY, and STOUT²⁾ obtained the same material and named it phytolaccatoxin. Hydrolysis of phytolaccatoxin gave glucose and xylose and aglycone, phytolaccagenin (V), $C_{31}H_{48}O_7$, mp 317—318°.

In our study, saponin fraction obtained from the MeOH extract of the dried roots, previously yielded,³⁾ on hydrolysis in dioxane-hydrochloric acid, a mixture of five sapogenins, jaligonic acid,^{4,5)} phytolaccagenin,²⁾ 3-oxo-30-carbomethoxy-24-nor-olean-12-en-28-oic acid,⁶⁾ and two unknown compounds, one of which seems to be a new compound, and we propose the name phytolaccagenic acid for it.

Phytolaccagenic acid (I), $C_{31}H_{48}O_6$, mp 309—311°, $[\alpha]_D^{25} = +86.5^\circ$ (c=0.4 in EtOH), $\lambda_{max}^{EtOH} 204 \text{ nm}$ (log ϵ , 3.79), gave pink color in LIEBERMANN-BURCHARD test and its IR spectrum showed a hydroxyl peak at 3400

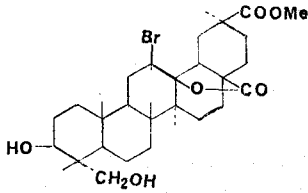
cm^{-1} , an ester peak at $1730cm^{-1}$, a carboxyl peak at $1700cm^{-1}$, and trisubstituted double bond peak at $825 cm^{-1}$. I was esterified on treatment with ethereal diazomethane to give a methyl ester (II), $C_{32}H_{50}O_6$, mp 149~151°, IR 1730 and $1710cm^{-1}$ (two methyl ester), and acetylation of I with acetic anhydride-pyridine



I~VII

	R_1	R_2	R_3	R_4	R_5
I :	H	H	H	H	Me
II :	H	H	H	Me	Me
III :	H	Ac	Ac	H	Me
IV :	H	Ac	Ac	Me	Me
V :	OH	H	H	H	Me
VI :	OH	H	H	Me	Me
VII :	H	H	H	H	H

gave a diacetate (III), $C_{36}H_{52}O_8$, mp 138–142°, IR 1738 and 1240 cm^{-1} (acetate), which failed to crystallize, but was homogeneous in TLC. Acetylation of II or methylation of III gave equally a methyl diacetate (IV), $C_{36}H_{54}O_8$, mp 100–103°. IR 1730 and 1235 cm^{-1} (acetate).



VIII

The presence of one double bond in I was shown by positive tetranitromethane color test and by the consumption of one mole of perbenzoic acid by IV.

The presence of one carbomethoxyl group in I was also shown by micro-ZEISEL method. On treatment with Br_2 -HOAc, I gave a monobromo- γ -lactone(VIII), mp 238°, IR 1770 cm^{-1} (γ -lactone) and 1725 cm^{-1} (methyl ester). This suggested that I belongs to the group of oleanane series having a carboxyl group at C-17 and a double bond at 12 : 13 position as in oleanolic acid.

The mass spectra of I and II show typical retro-DIELS-ALDER fragmentation patterns expected for olean-12-enes and a striking similarity in the ratio and an identity of position of the peaks up to m/e 310 compared to phytolaccagenin (V) and its methyl ester (VI).^{5,7)} The mass spectral analysis clearly show the C-20 position of carbomethoxyl group.

Phytolaccagenic acid (I) on treatment with sodium periodate failed to consume the reagent and starting material was recovered. This result indicates that I has no vicinal glycol, and from the biogenetic standpoint,

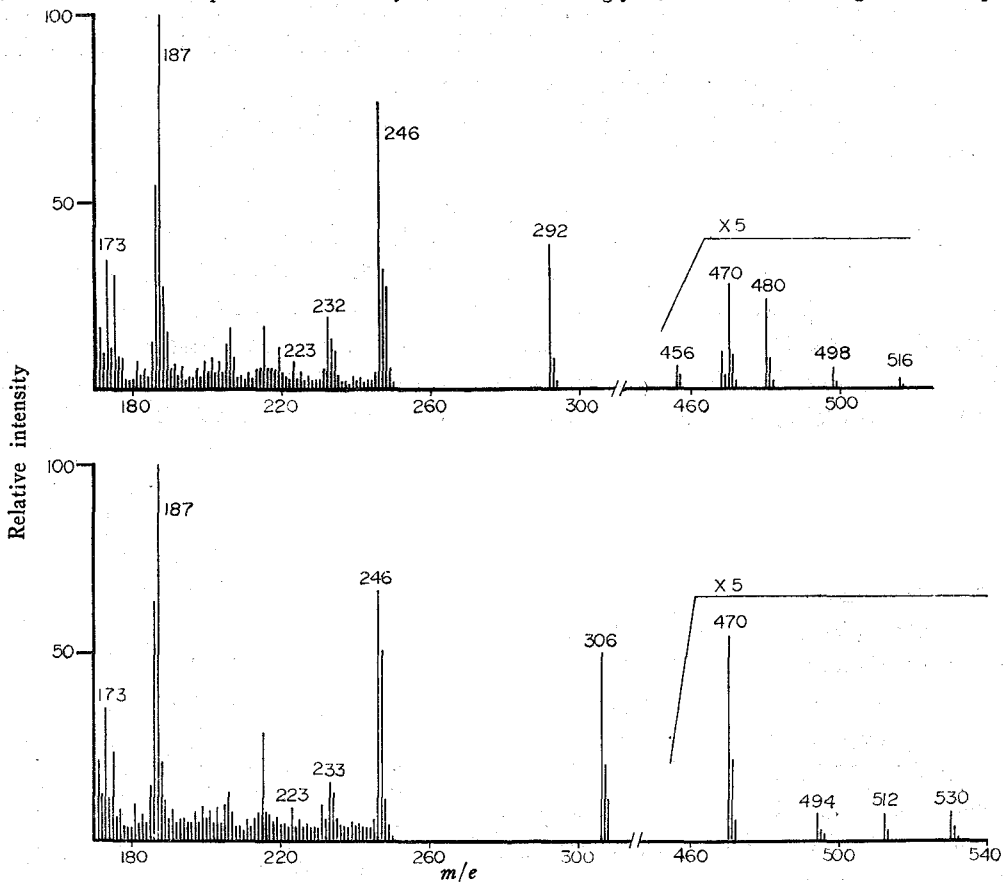


Fig. 1. Mass spectra of phytolaccagenic acid(upper) and its methyl ester(lower).

it is expected that I differs from V only in the lack of a hydroxyl group at C-2. On the basis of the preliminary experiments, I is supposed to be 3 β ,23-dihydroxy-30-carbomethoxy-olean-12-en-28-oic acid.

One of us⁸⁾ has recently isolated a new compound, esculentic acid, from *Phytolacca esculenta*. Physical properties of II are almost identical with those of dimethylesculentate and hydrolysis product(VII) of I is doubtless identical with esculentic acid. It has been reported that TLC behavior of the second unknown compound was identical with that of the product formed from I by alkali hydrolysis⁹⁾. It is, therefore, concluded that phytolaccagenic acid (I) is 30-methylesculentate and the second unknown compound is esculentic acid (VII). Detailed work leading to the complete structure elucidation of esculentic acid and phytolaccagenic acid will be reported elsewhere.

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