

Rubusic Acid, A New Triterpene from *Rubus moluccanus* Linn.

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Occurrence of a new pentacyclic triterpene, rubusic acid has been observed in the whole plant of *Rubus moluccanus* (Fam. Rosaceae). The present communication concerns with its structure elucidation. *R. moluccanus* is a plant of tropical India, leaves and fruits of which are used as a remedy for the nocturnal micturation of children¹. Rubusic acid was isolated from the ethanol extract of the whole plant of *R. moluccanus* previously defatted with petroleum ether (b.p. 60–80°) from which β -sitosterol was obtained. The acidic material from ethanolic concentrate, after several charcoalisations, was treated with ethereal solution of diozomethane. The methyl ester was obtained by chromatography (alumina) and purified by crystallisation from CHCl_3 -petroleum ether mixture (1 : 3) as light needles, $\text{C}_{31}\text{H}_{50}\text{O}_4$ ($M^+ = 486$ from mass spectrometry), m.p. 215–17°, $[\alpha]_D^{25} = +55^\circ$ (CHCl_3) from which rubusic acid $\text{C}_{30}\text{H}_{48}\text{O}_4$, m.p. 265–70° was obtained on ethanolic alkali hydrolysis.

Methyl rubusate showed positive Libermann Burchard and tetranitromethane tests: It showed no u.v. absorption above 210 $m\mu$ and I.R. absorptions were at 3450 ($-\text{OH}$), 1730 (COOCH_3), 1640 (unsaturation), 1410 ($\text{C}-\text{CH}_3$), 1380 ($\text{C} \begin{smallmatrix} \text{CH}_3 \\ \diagup \\ \text{CH}_3 \end{smallmatrix}$), 1170 ($\text{C}-\text{O}-\text{C}$) and 815 cm^{-1} (trisubstituted double bond). The N.M.R. spectrum of the methyl ester in CDCl_3 solution (60 mc) exhibited signals of seven tertiary methyl groups at 0.75, 0.83, 0.95, 1.01, 1.06, 1.10 and 1.15 ppm, a single proton signal at 2.72, methyl ester at 3.65 and a vinylic proton signal at 5.31 ppm. On treatment with acetic anhydride and pyridine (both at room temp. and under reflux) methyl rubusate formed a monoacetate, m.p. 144–45°, $\text{C}_{33}\text{H}_{52}\text{O}_5$, $[\alpha]_D^{25} +21^\circ$ (CHCl_3) [$D_{max}^{u,iol}$ 3400 ($-\text{OH}$), 1740 and 1250 cm^{-1} (O.COCH_3)] and a diacetate m.p. 195°, $\text{C}_{35}\text{H}_{54}\text{O}_6$ [$\alpha]_D^{25} +40^\circ$ (CHCl_3) with acetic anhydride and perchloric acid [$D_{max}^{u,iol}$ 1725 and 1260 cm^{-1} (OCOCH_3)]. Methyl rubusate failed to react with periodic acid.

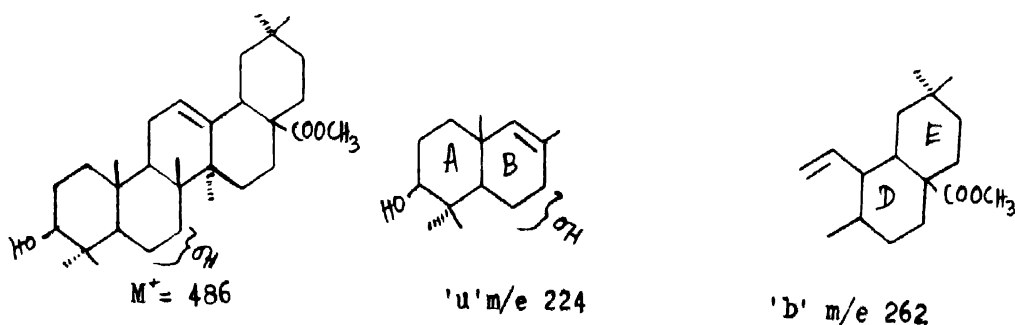
Acetyl methyl rubusate m.p. 144–45° furnished an acetyl monoketonic ester, $\text{C}_{33}\text{H}_{50}\text{O}_6$, m.p. 248–50° [$\alpha]_D^{25} +39^\circ$ (CHCl_3)], on oxidation with chromic acid and acetic acid, [λ_{max} 290 $m\mu$ ($\log \epsilon$ 1.9), $D_{max}^{u,iol}$ 1720 cm^{-1} (six membered ketone)]. The ketone did not form any oxime. Methyl rubusate on oxidation with chromic acid and acetic acid afforded an isolated diketonic ester, which did not show any ferric chloride colour reaction [λ_{max} 287 ($\log \epsilon$ 2.1)], monoxime m.p. 215°.

Again, acetyl monoketonic ester on oxidation with selenium dioxide in dioxan gave a diketonic ester, [positive ferric chloride colour reaction, λ_{max} 288 $m\mu$ $\log \epsilon$ 4.1]. Acetyl monoketonic ester m.p. 248–50° underwent Barton's modification² of Wolff-Kishner reduction

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and yielded oleanolic acid (from m.m.p., T.L.C. and IR with authentic sample). Thus rubusic acid is a hydroxy oleanolic acid and as it is not 1 : 2 or 1 : 3 diol, therefore the second hydroxyl must be situated in ring other than A.

The mass fragmentation pattern (species 'a' and 'b') of methyl rubusate follows that of oleanolic acid^{3,4} and shows without ambiguity that the second hydroxyl is situated in ring B, the position of which is either C-6 or C-7.



Methyl rubusate is neither identical with sumnresinolic acid methyl ester⁵ (which is 6-hydroxy oleanolic ester) nor can it be converted to this compound and acetylation of methyl rubusate with acetic anhydride in presence of perchloric acid gives a diacetate and not an unsaturated compound. These facts establish that rubusic acid is 7-hydroxy oleanolic acid. The resistance towards acetylation indicates that this hydroxyl group is in all probability axially oriented. Therefore rubusic acid is 3- β -7 α -dihydroxyolean-12-en-28-oic acid.

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