

Isolation and Structure Elucidation of New Pentacyclic Triterpene Acid from the Leaves of *Rubus ellipticus*

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Abstract – A new pentacyclic triterpene acid, elliptic acid was isolated from the ethanolic extract of the leaves of *Rubus ellipticus*. On the basis of physical evidences coupled with chemical investigations, the structure of elliptic acid was given as, 3,7,11-trihydroxy ursolic acid.

Key words – *Rubus ellipticus*, Rosaceae, 3,7,11-trihydroxy ursolic acid.

Introduction

In continuation of our investigations on the chemical constituent of different species of the genus *Rubus* (Ganguly, 1970; Mukherjee *et al.*, 1984), we wish to report in this communication the isolation and structure elucidation of a new pentacyclic triterpene acid, elliptic acid (1) from the leaves of *Rubus ellipticus*.

Results and Discussion

The crude acid obtained from the ethanolic extract of the defatted plant material was esterified with diazomethane. The methyl ester (2), $C_{31}H_{50}O_5$, m.p., 162-63° (α_D +53° (CHCl₃) on hydrolysis with ethanolic alkali, regenerated pure elliptic acid (1), $C_{30}H_{48}O_5$, m.p. 271-72° (α_D +48° (MeOH). This acid showed positive Liebermann-Buchard test for triterpene and found homogenous in T.L.C. The IR spectrum of the methyl ester showed the presence of hydroxyl and ester carbonyl groups. The appearance of three peaks in the region 1400-1350 cm⁻¹ and two peaks in the region 1330-1240 cm⁻¹ in the IR spectrum of the ester indicated that it was probably an ursane derivative (Snatzke *et*

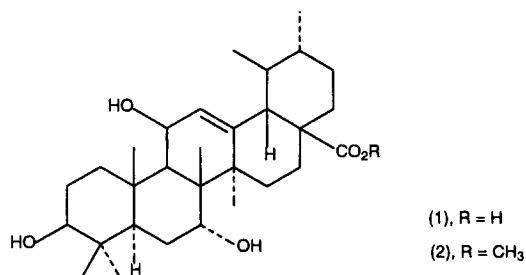
al., 1962). Methyl elliptate formed two acetyl derivatives; the diacetyl derivative was formed easily at room temperature with acetic anhydride and pyridine, whereas, the triacetyl derivative was formed under acidic condition using acetic anhydride and perchloric acid (Toennies and Elliot, 1935; Barton and Praitt, 1950, 1953) which showed that one of the three hydroxy groups in elliptic acid is sterically hindered. Since methyl elliptate failed to react with periodic acid it was not a 1,2-dihydroxy compound. The IR spectrum of diacetate, $C_{35}H_{54}O_7$, m.p. 282-84° showed the presence of a hydroxyl group and acetyl carbonyl group. (ν^{nujol} 3450 and 1725 cm⁻¹). The IR spectrum of the triacetate $C_{37}H_{56}O_8$, m.p. 293-94° gave peak at ν^{nujol} 1720 and 1690 cm⁻¹ showing the presence of acetyl carbonyl and absence of hydroxy function. Diacetyl methyl elliptate on Sarett oxidation furnished diacetyl mono ketonic ester, $C_{35}H_{52}O_7$, m.p. 262-63° which showed bands at 1735, 1720 and 1260 cm⁻¹ in IR spectrum. It did not undergo borohydride reduction nor showed any Zimmermann color reaction. On the other hand methyl elliptate on oxidation with Cr O₃-acetic acid complex afforded the corresponding triketo compound, $C_{31}H_{44}O_5$, which gave a negative ferric chloride test and a positive Zimmermann color reaction. The UV spec-

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trum of this keto compound showed maximum absorption at λ_{\max} 250 nm indicating the presence of an α,β unsaturated keto compound. The above triketone on borohydride reduction gave monoketone $C_{31}H_{48}O_5$, m.p. 256-59° identical with the hydrolysis product of 3,11-diacetyl monoketonic ester of elliptic acid. This monoketone neither formed an oxime nor showed Zimmermann color reaction. Thus elliptic acid is a trihydroxy carboxylic acid. So, two of the three secondary hydroxyl groups are easily acylable and one of these two is placed at C-3 position of a pentacyclic triterpene skeleton. The second easily acylable hydroxyl group should be at C-11 as the triketone compound gave a UV characteristic of an α,β unsaturated carbonyl compound. Since unsaturation is at 12-13, the second unhindered hydroxyl is, therefore, placed at C-11. The third hydroxyl group which is hindered and cannot be acetylated under normal condition is either at C-6 or C-7 position in ring B of a pentacyclic triterpene skeleton. The NMR spectrum of the methyl ester revealed the presence of one olefinic hydrogen at δ 5.27 and one methyl ester group at δ 3.61. Besides these there is a three proton signal at δ 3.14 which is attributed to the methine proton of C-3, C-7 and C-11 hydroxyl groups. Mass spectral examination of methyl elliptate indicated a molecular weight of 502, in agreement with

molecular formula $C_{31}H_{50}O_5$. Some other important peaks are at 487, 484, 466, 448, 444. Retro Diels-Alder fragmentation of the molecule led to ion species at m/z 278. Loss of 59 mass units ($COOCH_3$) from 278 led to the formation of a peak at m/z 219. Further, the mass spectrum of keto methyl elliptate showed intense peak at m/z 317.

On the basis of the above the structure of the above compound may be represented as:

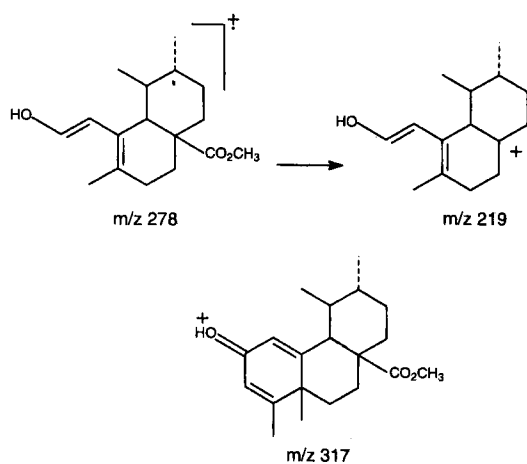


The ^{13}C -NMR data of elliptic acid (1), is in good agreement with the other ursolic acid derivative reported earlier (Yadava and Khare, 1995). ^{13}C -NMR: δ 38.2 (C-1), 25.3 (C-2), 81.2 (C-3), 42.5 (C-4), 49.0 (C-5), 18.3 (C-6), 76.2 (C-7), 41.0 (C-8), 50.2 (C-9), 37.3 (C-10), 74.8 (C-11), 122.6 (C-12), 144.4 (C-13), 43.4 (C-14), 27.7 (C-15), 24.6 (C-16), 46.5 (C-17), 42.3 (C-18), 45.9 (C-19), 30.4 (C-20), 33.4 (C-21), 32.6 (C-22), 28.2 (C-23), 17.6 (C-24), 15.6 (C-25), 17 (C-26), 26.0 (C-27), 178.2 (C-28), 29.2 (C-29), 21.3 (C-30).

The above structure was further confirmed by the fact that the triketone obtained from methyl elliptate was found identical in all respect with the product obtained by the oxidation of 3-acetyl-7-keto methyl rubitate with chromic acid and acetic acid on steam bath and then saponification followed by Sarett oxidation of the product.

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