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# Quassinoids and Their Chemotaxonomic Significance

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The quassinoids are a group of complex, highly oxygenated, degraded triterpene mostly found in *Simaroubaceae* family. Two quassinoids (degraded triterpenes), **1** and **2** were isolated first time from the stem bark of *Ailanthus excelsa*. Compound **1** is $C_{19}$ quassinoid. $C_{19}$ quassinoid derived biogenetically from a $C_{20}$ quassinoid, *via* a 1,2 – dioxo derivative. The structural elucidation is based on the analysis of spectroscopic data. Interest in these quassinoids has increased enormously in recent years due in part to the finding of the American National Cancer Institute that these compounds display marked antileukamic activity. The ways in which plants interact with other organisms in an environment are complex. *Ailanthus* also produces toxins in its root, bark and leaves. These toxins inhibit the growth of other plants. The isolated quassinoids are currently being studied as a possible source of a natural herbicide. Extracts of this plant have anti-insect activity and anti-tuberculosis activity.

*Keyword*: *Ailanthus excelsa*, Quassinoid, Polyandrol, Glaucarubolone.

## 1. Introduction

Medicinal plants constitute a source of raw materials for both traditional systems of medicine (e.g. Ayurvedic, Chinese, Unani, Homeopathy, and Siddha) and modern medicine. Nowadays, plant materials are employed throughout the industrialized and developing world as home remedies, over-the-counter drugs, and ingredients for the pharmaceutical industry. Most rural populations, especially in the developing world, depend on medicinal herbs as their main source of primary health care. The therapeutic potential of a herbal drugs depends on its form: whether parts have a plant, or simple extracts, or isolated active constituents. Herbal remedies consist of portions of plants or unpurified plant extracts containing several constituents, which often work together synergistically.

*Ailanthus excelsa* Roxb. is a large deciduous tree belonging to the family Simaroubaceae, and commonly known as "Mahanimb". The plant is distributed in Asia, north Australia and is indigenous to central and southern India[1]. Chemical examination of *A. excelsa* has been carried out by several groups of workers, which led to the isolation of quassinoids[2-7], alkaloids[8], and terpenoids[9]. Since quassinoids are reported to possess antileukemic, antiviral, antimalarial, amoebicidal, anti-inflammatory, antifeedant, antifungal and insecticidal properties[10-11].
We were interested in the isolation of minor quassinoids present in *A. excelsa* and environmental impact on them. We have previously reported two new quassinoids and estabilish relative stereochemistry of one of them[7,12].

## 2. Material and Methods

The stem-bark of *Ailanthus excelsa* was collected in September 2001 from Kukrail Reserve Forest, Lucknow. The identification of the plant was carried out by Dr. S.P. Jain, Botany Department, CIMAP, Lucknow, where a voucher specimen has been deposited.

10 kg of the dried powdered bark of *A. excelsa* was exhaustively extracted with cold MeOH. The MeOH extract was evaporated *in vacuo* to give residue (220 g). The residue was fractionated by $CHCl_3$, EtOAc and water. The ethyl acetate fraction (8 g) was chromatographed on a column of silica gel with stepwise increases of MeOH content in $CHCl_3$ (1,2,3,5,10 and 20%). The 5% MeOH eluate was purified by preparative TLC (silica gel, $CHCl_3$: MeOH; 90:10), furnished polyandrol **(1,**20 mg**)** as solid m.p 191°C. The 7% MeOH eluate gave glaucarubolone (**2**, 15 mg) as a solid m.p. 258°c. These two compounds has been isolated first time from this plant.

**Acetylation of 1:** A solution of 10 mg of **1** in 1 ml of pyridine was treated with 2 ml of acetic anhydride and the reaction mixture left at room temperature. The reaction was monitored on TLC and after 48 hr when the reaction was complete; the reaction mixture was diluted with 25 ml of water and extracted with $CHCl_3$ (3x25 ml). The $CHCl_3$ extract was dried and evaporated to give a residue which was purified by silica gel prep. ($CHCl_3$: MeOH, 96 : 4) to yield triacetate **3** (6 mg) as a solid, mp 1620C, [α]23D + 210 ($CHCl_3$ ; c 0.75), IR $\nu_{max}^{KBr}$ cm-$^{1}$: 1727, 1720, 1710, 1265, 1050, ESMS m/z: 529 [M+Na]+, 545 [M+K]+, EIMS m/z: 506 [M]+, 409 [M+ -97], 367, 324, 246, 229, 201, 173, 145, 97, 69, 54, 43, $C_{25}H_{30}O_{11}$.

All melting points were determined in open capillaries and are uncorr. $^{1}H$ and $^{13}C$ NMR spectra were recorded at 300 MHz instrument using TMS as internal standard. The electrospray mass spectra (ESMS) were recorded on a MICROMASS QUATTRO II Triple Quadrupole Mass spectrometer. The samples (dissolved in appropriate solvent) were introduced into the ESI source through a syringe pump at the rate of 5 µl per min. The ESI capillary was set at 3.5 kV and the cone voltage was 40V. The spectra were collected in 6 s scans. TLC was performed on silica gel-G (Qualigen). The solvent system used for TLC was variying proportions of MeOH in $CHCl_3$ and spots were revealed by spraying with 50% sulfuric acid. The column chromatography (cc) was performed on silica gel 60-120 (Qualigen).

## 3. Results and Discussions:

The ethyl acetate fraction of the MeOH extract of the stem bark of A. excelsa afforded **1**, and **2** after column chromatography.The spectral data of the **1**, and **2** were in good agreement with those published in the literature[13-14] and also confirmed by synthesis of there acetate **3** and **4** respectively. The acetate of polyandrol **3** is being reported for the first time.

Genus *Ailanthus* is a rich source of quassinoids[15], and more than 60 quassinoids have been identified so far from this genus. Mostly The quassinoids are a group of complex, highly oxygenated, degraded triterpene biogenetically formed from triterpene apo-euphol or its 20 α-isomer apo-tirucallol. The triterpenoid biogenetic pathway for the quassinoids has been experimentally verified by using labelled mevalonate precursors[16-17].

Only a few $C_{19}$ quassinoids have been isolated from different parts of the genus *Ailanthus*. This is the first report of $C_{19}$ quassinoid from *Ailanthus excelsa*. $C_{19}$ quassinoids possessing the 1,2-seco-1-nor-6(5→10)-abeo-picrasan-2,5-olide skeleton. These may be derived biogenetically from a $C_{20}$ quassinoid, *via* a 1,2 –dioxo derivative.

Under oxidative conditions a 1,2 –dioxo compound, might undergo successively a C(1)-C(2) bond cleavage, decarboxylation, a contraction of the B ring and formation of the α,β-unsaturated γ-lactone to give $C_{19}$ quassinoids[18]. Polyandro (**1**) has been isolated from other Simaroubaceae plant *Castela polyandra*[13] but it has been isolated first time from genus *Ailanthus*.The presence of compound **1** in *Ailanthus excelsa* showed that other *Ailanthus* species also may contain known or novel $C_{19}$ quassinoids.

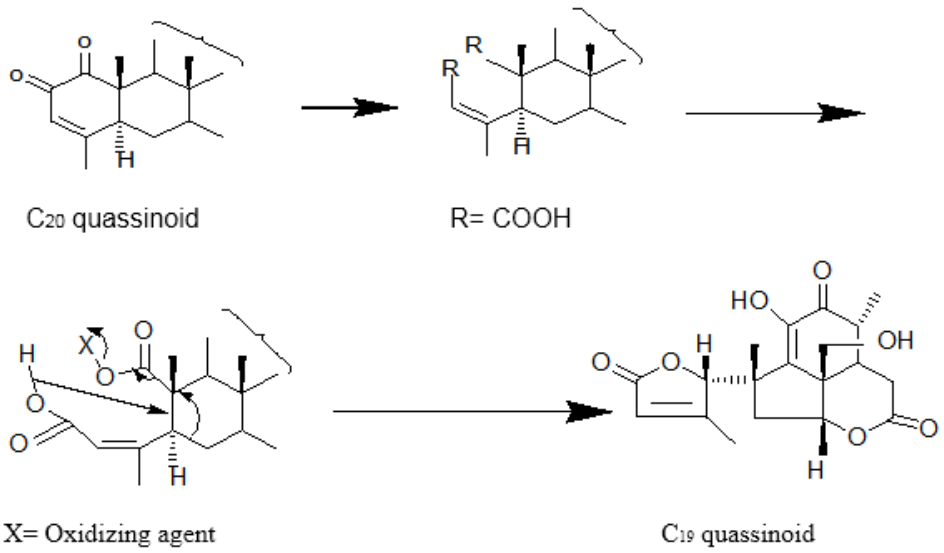
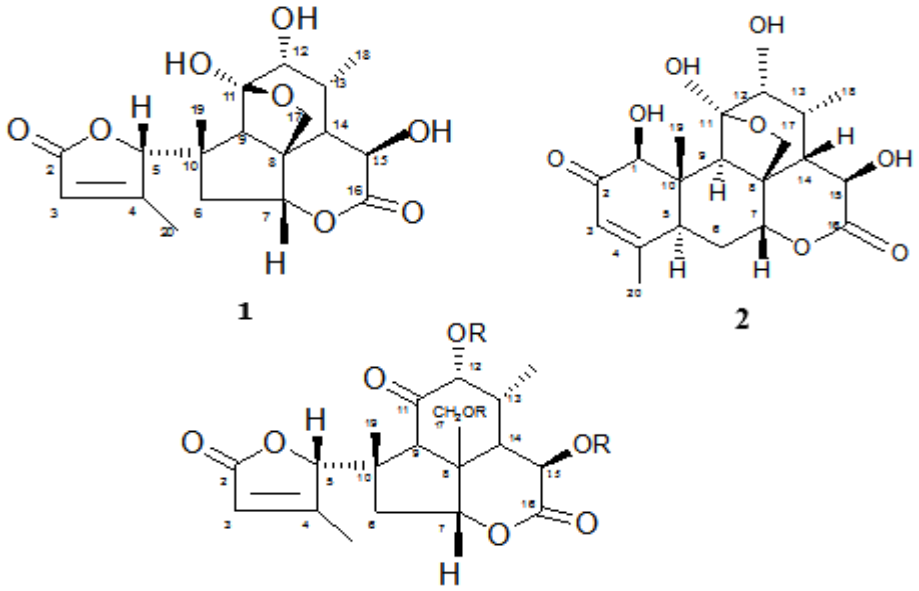



**Fig:** Potential biosynthesis pathway for conversion of $C_{20}$ quassinoid into $C_{19}$ quassinoid.



**1** **2**

3. R=COCH3, diacetate of polyandrol

Due to rapid growth of the *Ailanthus excelsa* and prolific seed production, it quickly escaped cultivation. The tree also produces toxins in its root, bark and leaves. These toxins inhibit the growth of other plants. The isolated quassinoids are so effective that they are currently being studied as a possible source of a natural herbicide[19]. These factors make the *Ailanthus* a very aggressive and invasive plant able to displace native trees and herb species. Extracts of this plant have anti-insect activity and anti-tuberculosis activity[7,19]. The aim of this study was to determine the chemical composition of compounds from the bark of ailanthus depending on the stage of plant development and climatic change. Finally, we concluded from these results that the qualitative and quantitative composition of the compounds of ailanthus strongly depends on the stage of plant development as well as on the climatic conditions including soil compositions. This is due to the climatic condition of the collection site of the sample. Climate of the site may help to generate the different compounds in the plants by biogenesis.

## 4. Acknowledgements

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