

SAPONINS AND SAPOGENINS XXV* - THE SAPOGENIN OF ACACIA
CONCINNA D.C. PODS AND THE CONSTITUTION OF ACACIC ACID

I.P. Varshney & K.M. Shamsuddin

Department of Chemistry, Aligarh Muslim University, Aligarh, India.

(Received 10 June 1964)

The pods of *Acacia concinna* D.C. by alcoholic extraction yields a colourless saponin, which on hydrolysis with sulphuric acid yields an acid genin, m.p.268-72°, diacetyl lactone m.p.235-36°. This acid has been identified as acacic acid (I)¹ by mixed melting point with authentic samples of acacic acid and its acetyl lactone respectively, (Cf. Acacic acid m.p.275-76°; acacic acid acetyl lactone m.p.235-36°)¹.

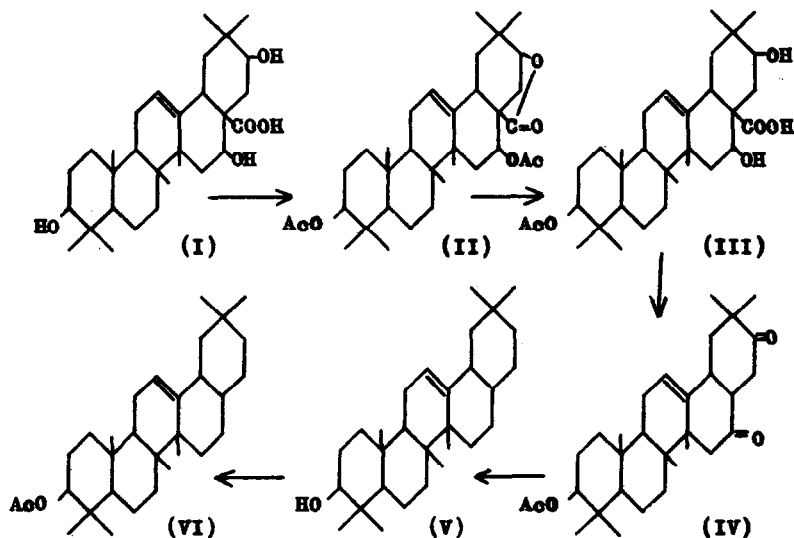
Acacic acid is a sapogenin of fairly common occurrence. Apart from the bark of *Acacia intsia*¹, it has also been reported in the bark of *Albizia lebbek*² and in the seeds of *Acacia intsia*³, *Acacia concinna*³, *Albizia stipulata*⁴ and *Albizia odoratissima*⁵. The preliminary studies fixed acacic acid as a trihydroxy monocarboxylic triterpenic acid of either tetracyclic

*Part XXIV - In the press.

or α -amyrin group*. Later, one of the authors^{6,7} on biogenetic grounds favoured a β -amyrin type structure and also proposed 3,16,21 trihydroxy-olean-12-ene-28-oic acid (I) structure for acacic acid. This paper describes the chemical evidences which support this formulation (I).

Acacic acid acetyl lactone (II) on treatment with methanolic hydrochloric acid (10%) on a water bath, gave a product m.p. 257-61° (III). The product (III) on oxidation (with chromic acid and pyridine in cold) furnished a neutral acetyl diketone m.p. 338-42° (IV) (Found: C, 76.50; 76.44; H, 8.97; 9.13; Calcd. for $C_{31}H_{46}O_4$: C, 77.13; H, 9.61) due to the formation of a β -ketonic acid which decarboxylates easily to yield a neutral diketone (IV), with the loss of one molecule of carbon dioxide. The ketone (IV) on Wolff-Kishner reduction again yielded a neutral product m.p. 183-88 (V) (Found: C, 84-20; H, 11.73, Calcd. for $C_{29}H_{46}O$: C, 84.40; H, 11.72). The product m.p. 183-88 (V) on acetylation with acetic anhydride and pyridine in cold gave an acetate m.p. 210-16° (VI). The products (V) and (VI) have been found to be identical with 28-nor β -amyrin (Nor-echinocystenol A) and its acetate respectively by mixed melting points with authentic samples obtained from echinocystic acid⁸.

*Z.Naim Ph.D. Thesis, Aligarh Muslim University, Aligarh, 1962 suggested it to have an α -amyrin structure carrying one primary and two secondary hydroxyl groups and a carboxyl group.



The formation of 28-nor β -amyrin (V) from Acacic acid (I) proves beyond doubt that acacic acid is a member of the β -amyrin group with one of the hydroxyl groups at C-3, carboxyl group at 28 and the double bond between C-12 and 13. The position of the second hydroxyl group was taken to be at C-21 due to the formation of a γ -lactone (II) in the acetylation process. Finally the position of the remaining i.e. the third hydroxyl group was indicated at C-16 or C-22 by the fact that the carboxyl group easily decarboxylates on oxidation due to the formation of a β -ketoic acid. Out of these two positions the third hydroxyl was finally fixed at

C-16 as acacic acid on periodic acid oxidation was recovered unchanged thereby eliminating position C-22 as it is adjacent to the 21-hydroxyl group. Therefore the constitution of acacic acid has finally been fixed as 3,16,21-trihydroxy olean-12-ene-28-oic acid (I).

Further work on the stereochemistry and conformation is in progress.

Thanks are due to the Council of Scientific and Industrial Research, New Delhi for the award of Junior Research Fellowship to one of the authors (K.M.S.).

REFERENCES

1. M.O. Farooq, I.P. Varshney and Z. Naim, Arch. der Pharm., **294**, 133-37, (1961).
2. H. Hasan, I.P. Varshney and S.A. Ahmad, Indian J. Pharm., **23**, 331-32, (1961).
3. M.O. Farooq, I.P. Varshney and Z. Naim, Arch. der Pharm., **295**, 12-14, (1962).
4. I.P. Varshney, Symposium on "Chemistry of Natural Products" Allahabad, 1964, Proc. Nat. Acad. Sci. India. (In the press).
5. I.P. Varshney and M.S.Y. Khan, Unpublished results.
6. I.P. Varshney, Intern. Symposium on "Natural Products", IUPAC., Bruxelles, 1962, Resume des Communs.
7. I.P. Varshney, Leguminosae Saponins, Symposium on Glycosides & Saponins", Calcutta 1964, C.S.I.R., (India), (In the press).
8. I.P. Varshney, Thesis. Dr. d'Etat, Université de Paris, Soutenue le 21 December, 1956, Ch. Sannicé, H. Lapin & I.P. Varshney, Bull. Soc. Chim. France, 1957, 1440-44.