BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 43 446—447 (1970)

Study of the Sapogenins from *Albizzia lebbek* Benth. Seeds

I. P. VARSHNEY and Geeta BADHWAR

Department of Chemistry, G. S. Technological Institute, Indore-3, India

(Received March 25, 1969)

The seeds of *Albizzia lebbek* Benth. from Madhya Pradesh have been found to contain a mixture of saponins which on hydrolysis gives echinocystic acid (I), oleanolic acid (II) as major sapogenins and an unidentified sapogenin (not albigenin) in traces. The albigenic acid (III) earlier reported to be present has been shown to be an alcoholic hydrochloric acid isomerisation product of echinocystic acid.

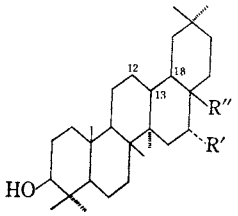
The seeds and pods of *Albizzia lebbek* Benth. have been found to be a rich source for saponin and sapogenin contents.[1,2] Varshney *et al.*[1,2] have isolated a saponin mixture from the seeds collected from Utter Pradesh (U. P.), which on hydrolysis with 10% sulphuric acid yields three sapogenins, echinocystic acid (I), oleanolic acid (II) and a third sapogenin in trace (in the proportion 75: 20: trace).

Later Barua and Raman[3] studied the whole beans of *Albizzia lebbek* Benth. (containing pods and seeds), collected from Bengal, and reported that the hydrolysis of the crude saponin with hydrochloric acid in ethanol yields four sapogenins, echinocystic acid (I), oleanolic acid (II), albigenic acid (III) and albigenin (IV). It may be noted that the two extra sapogenins (albigenin and albigenic acid) reported by these authors[3] may be either present in pods or in the seeds from Bengal and absent in the seeds from U. P. studied by Varshney *et al.*,[1,2] or may be the artifact of alcoholic hydrochloric acid hydrolysis. To clarify this, the present work has been undertaken.

1) Ch. Sannié, H. Lapin and I. P. Varshney, *Bull. Soc. Chim. Fr.* **1957**, 1440.

2) I. P. Varshney, Thesis, Dr. d'Etat, Etude des Sapogénines d'*Albizzia lebbek* Benth., Soutenue 1956, Université de Paris, France.

3) A. K. Barua and S. P. Raman, *Tetrahedron*, **7**, 19 (1959); *ibid.*, **18**, 155 (1962).



I R′=OH; R″=COOH; Δ^{12-13}
II R′=H; R″=COOH; Δ^{12-13}
III R′=OH; R″=COOH; Δ^{13-18}
IV R′=O; R″=H; Δ^{13-18}

Finely powdered *Albizzia lebbek* Benth. seeds collected from Madhya Pradesh (M. P.) were defatted with petroleum ether and exhausted with ethanol. The ethanolic extract on concentration and subsequent treatment in the usual manner gave a saponin which was purified by dissolving in a small quantity of methanol, and by adding to large amounts of ether/acetone a number of times. This caused precipitation of the saponin as a light brown coloured powder satisfying all the tests for saponins.

Half of the saponin was hydrolyzed with 10% sulphuric acid by heating on a boiling water bath for one hour and then refluxing for another hour (*cf.* Varshney *et al.*[1,2]), and the remainder of the saponin with ethanolic hydrochloric acid (using the same procedure as that of Barua and Raman[3]). The sapogenins obtained by sulphuric acid hydrolysis on thin layer chromatography showed three spots, two present in major quantity and the third one in trace only, *viz.* echinocystic acid (I), oleanolic acid (II) and an unidentified one, as earlier reported by Varshney *et al.*[1,2] The sapogenins obtained by ethanolic hydrochloric acid hydrolysis showed the presence of four prominent spots, corresponding to echinocystic acid (I), oleanolic acid (II), albigenic acid (III), and the fourth may be identical with albigenin (IV), confirmed by alongside chromatography (TLC) with authentic samples. This conclusively showed that albigenic acid (III) and most possibly albigenin (VI) are artifacts formed by the ethanolic hydrochloric acid hydrolysis of the saponin as they are not obtained in the sulphuric acid hydrolysis product of the same saponin. During alcoholic hydrochloric acid hydrolysis the migration of the double bond takes place from 12—13 position to 13—18 position yielding albigenic acid (III) from echninocystic acid (I) (I → III). This type of migration is not rare and was earlier reported by Spring *et al.*[4] All the four sapogenins were separated by repeated column chromatography on silica gel and identified by melting points, (mp obtained (I) 306—308°C (II) 305—306°C, (III) 280—281°C and (IV) 224—226°C; lit. echinocystic acid, 305—312°C, oleanolic acid, 310°C, albigenic acid, 280—281°C and albigenin, 226—228°C).

The possibility of the shifting of the double bond in the case of albigenic acid (III) was ruled out by Barua and Raman[3] by heating echinocystic acid (I) with ethanolic hydrochloric acid. It might be possible that such migration might not have taken place in their case due to some reason such as the variation in the conditions and concentration *etc.* as the experimental details of such experiment are not given.[3] In our repeated attempts, when free echinocystic acid (I) was heated with ethanolic hydrochloric acid (20%) it always yielded a number of products (3 new products and one starting material *i.e.* echinocystic acid) as shown by the thin layer chromatography. Starting with TLC pure echinocystic acid, the major product corresponded with albigenic acid (III) on thin layer chromatography. Therefore albigenic acid (III) is nothing but an alcoholic hydrochloric acid isomerisation product of echinocystic acid (I) and is not present in *Albizzia lebbek* plant, seeds or pods either as free genin or as saponin.

The albigenin (IV) is present in very small quantities in ethanolic hydrochloric acid hydrolysis product only, and this can also be a product of alcoholic hydrochloric acid isomerisation and probably some type of oxidation is taking place in the hydrolysis process itself, which might be giving rise to 16-keto acid by the partial oxidation of the echinocystic acid giving rise to a β-ketonic acid which decarboxylates in the hydrolysis process and the migration of the double bond taking place simaltaneously yielding albigenin (IV). It might also be possible that the third sapogenin (unidentified) present in trace in sulphuric acid hydrolysis product might be isomerising with ethanolic hydrochloric acid hydrolysis process yielding albigenin (IV). Therefore the aqueous sulphuric acid is a better hydrolyzing agent for saponins than alcoholic hydrochloric acid as the latter brings about isomerisation as reported in this paper and by Spring *et al.*[4] and some times corresponding ester is also formed.[5,6]

Thanks are due to the Chemical Research Committee of the Council of Scientific and Industrial Research, New Delhi, for the award of a junior research fellowship to one of the authors (G. B.) and to the authorities of the Shri Govindram Seksaria Technological Institute, Indore for the facilities.

4) G. Brownlie, M. B. E. Fayez, F. S. Spring, R. Stevenson and W. S. Strachan, *J. Chem. Soc.*, **1956**, 1377.

5) C. Djerassi, Festeschraft Arthur Stoll, (Brikhauser, Basal) 1957, 330.

6) I. P. Varshney, *Indian J. Chem.*, **7**, 446 (1969).