

# ISOLATION AND STRUCTURE OF PUTROLIC ACID—A NEW TRITERPENIC SECO-ACID FROM THE STEM-BARK OF PUTRANJIVA ROXBURGHII\*

G. R. CHOPRA, A. C. JAIN AND T. R. SESHADRI  
Department of Chemistry, University of Delhi, Delhi-7

**R**ECENTLY, four new triterpenes, viz., putrone, putrol, putranjivic acid and methyl putranjivate besides  $\beta$ -amyrin, its palmitate and stigmasterol were isolated by us from the leaves of *Putranjiva roxburghii* Wall (N.O. *Euphorbiaceae*).<sup>1</sup> We report here the isolation and constitution of a new triterpenic seco-acid, putrolic acid from the stem-bark.

Air-dried stem-bark was extracted successively with boiling benzene and alcohol. The alcoholic extract after concentration gave more benzene soluble material. Both were mixed and found to contain mostly triterpenic components. After saponification, they could be separated into a neutral fraction soluble in ether and insoluble colourless gelatinous precipitate. The former when examined by column chromatography over neutral alumina gave a low melting hydrocarbon (0.8%), friedelin (0.006%; identity confirmed by comparison with authentic sample kindly supplied by Professor P.R. Jefferies), a mixture of terpenic ketones (0.02%) reducible by LAH and stigmasterol (0.015%). The insoluble precipitate was purified better by chromatography after acidification and treatment with diazomethane. It yielded a crystalline methyl ester which on hydrolysis gave putrolic acid (0.5%). In order to make sure if it was present free or as ester, the benzene extracts were subjected to silica-gel column chromatography without prior saponification and putrolic acid was obtained in almost the same yield. It crystallised from  $\text{CHCl}_3$ -MeOH mixture as colourless crystals, m.p. 220–22°;  $[\alpha]_D + 21.3^\circ$  (C, 0.475)<sup>†</sup>;  $R_f$  0.6 in solvent B, 0.5 in F, 0.3 in G;  $\nu_{\text{max}}$  (nujol) 3500 (OH) and 1718  $\text{cm}^{-1}$  (C=O). The elemental analysis

of this and its derivatives showed the mol. formula to be  $\text{C}_{30}\text{H}_{52}\text{O}_3$ . Either with diazomethane or with methanol containing a trace of acid catalyst, it readily forms methyl ester which is the most satisfactory derivative for constitutional studies. It crystallises from  $\text{CHCl}_3$ -MeOH mixture as colourless long needles, m.p. 175–76°;  $[\alpha]_D - 8.3^\circ$  (C, 1.204);  $R_f$  0.4 in solvents A and D, and 0.8 in E; no colour with t.n.m.;  $\nu_{\text{max}}$  (KBr) 1730  $\text{cm}^{-1}$  (ester C=O);  $\delta(\text{CDCl}_3)$ : 3.90 p.p.m. (s, 3H of  $\text{CO}_2\text{CH}_3$ ). Elemental analysis and mass spectrum determined its mol. formula as  $\text{C}_{31}\text{H}_{54}\text{O}_3$  ( $M^+$  474). The n.m.r. spectrum of methyl putrolate showed that it is a saturated molecule having 7–8 methyl groups ( $\delta$  0.84–1.28 p.p.m.) and a secondary alcohol ( $\delta$  4.2 p.p.m., multiplet of one proton of CHOH). The presence of an alcoholic group was confirmed by preparing (i) methyl O-acetyl putrolate, m.p. 140–41°;  $[\alpha]_D + 19.0^\circ$  (C, 1.04);  $R_f$  0.8 in solvents A and D;  $M^+$  516; mol. formula  $\text{C}_{33}\text{H}_{56}\text{O}_4$ ;  $\nu_{\text{max}}$  (KBr) 1760  $\text{cm}^{-1}$ ;  $\delta(\text{CDCl}_3)$ : 2.18 (s, 3H of  $\text{OCOCH}_3$ ), 3.79 (s, 3H of  $\text{CO}_2\text{CH}_3$ ), 5.05 p.p.m. (m, 1H of CHOAc), and (ii) O-tosyl derivative, m.p. 141–42°;  $[\alpha]_D - 27.6^\circ$  (C, 1.09);  $R_f$  0.70 in solvent A and 0.75 in D; mol. formula  $\text{C}_{38}\text{H}_{60}\text{SO}_5$ . The secondary nature of the alcoholic group was shown by Jones' oxidation of methyl putrolate to form methyl oxoputrolate, m.p. 152–54°;  $[\alpha]_D + 24^\circ$  (C, 1.0);  $R_f$  0.9 in solvent A and 0.8 in D;  $M^+$  472; mol. formula  $\text{C}_{31}\text{H}_{52}\text{O}_3$ ;  $\nu_{\text{max}}$  (nujol) 1757  $\text{cm}^{-1}$  (C=O);  $\delta(\text{CCl}_4)$ : 3.82 (s, 3H of  $\text{CO}_2\text{CH}_3$ ), 2.67 p.p.m. (m, 2H of  $\text{CH}_2$  next to keto), no CHO signal. The molecular formula, the absence of unsaturation (lack of t.n.m. test) and the presence of OH and  $\text{CO}_2\text{H}$  groups in putrolic acid show that it is a triterpenic seco-acid having four rings (I).

That putrolic acid is an  $\alpha$ -hydroxyacid is shown by the following facts. (i) The n.m.r. spectrum of methyl putrolate (II) shows no signals for  $\alpha$ -methylene group in the region  $\delta$  2.3–2.5 p.p.m. (ii) The i.r. spectrum of methyl oxoputrolate showed only one carbonyl frequency which behaviour is reminiscent of  $\alpha$ -keto esters.<sup>2</sup> (iii) LAH reduction of methyl putrolate gives a 1,2-diol (III) (m.p. 212–14°;  $R_f$  0.1 in solvent A and 0.3 in C; mol. formula

\* This work was presented by one of us (A.C.J.) at the Indo-Soviet Symposium held at Tashkent during Sept. 18–20, 1968.

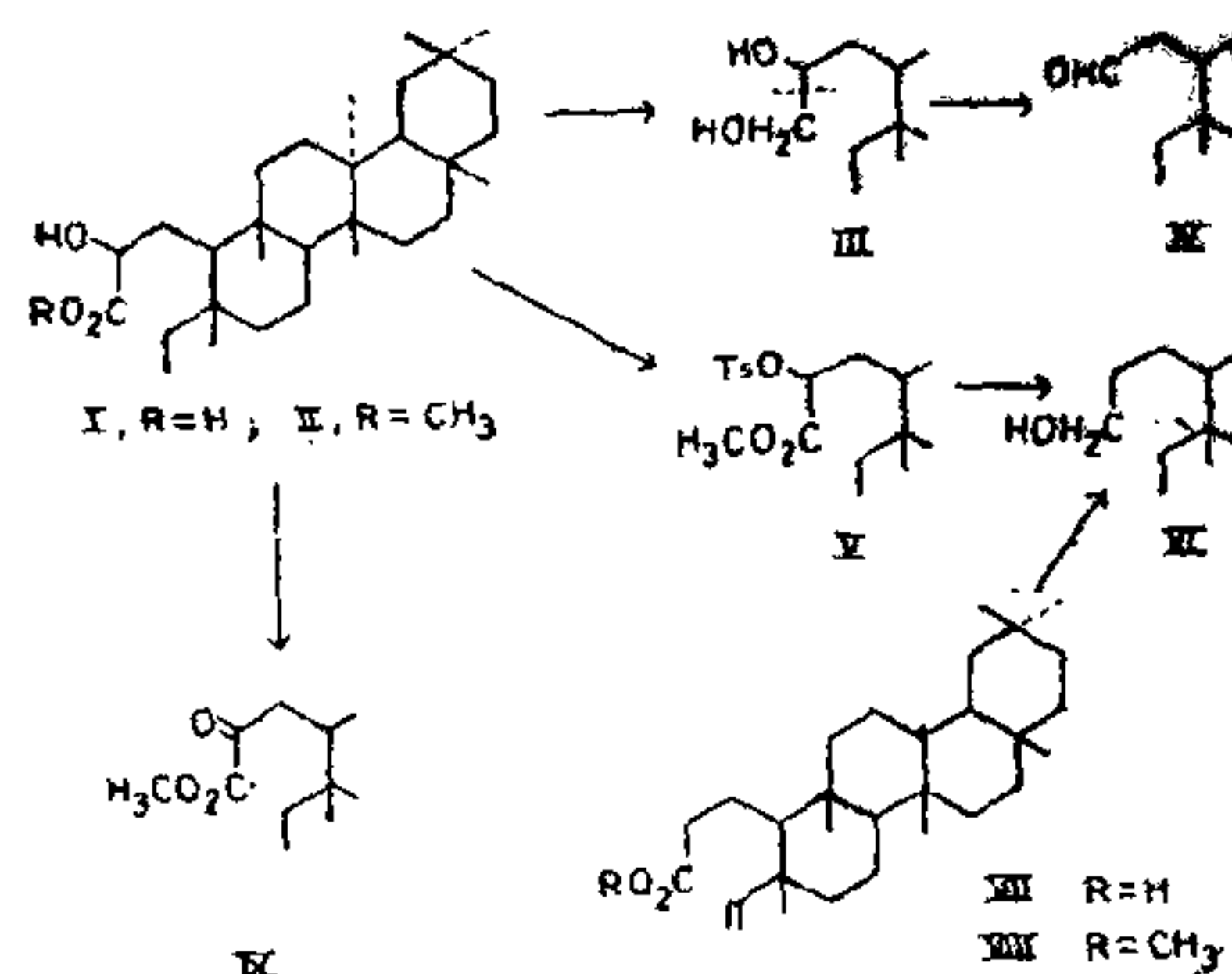
<sup>†</sup>  $[\alpha]_D$  values are in chloroform solution at 25° and concentration (c) in g/100 ml. All  $R_f$  values recorded in this paper are on t.l.c. on silica-gel using one of the following solvents. (A) Benzene, (B) Ethyl acetate : light petroleum (1 : 4), (C) Chloroform, (D) Light petroleum : chloroform (1 : 1), (E) Light petroleum : methanol (98 : 2), (F) Ethyl acetate : benzene (1 : 9), (G) Chloroform : methanol (85 : 15). Satisfactory analytical figures were obtained for the compounds where molecular formulae are shown.



$C_{30}H_{54}O_2$ ) which undergoes cleavage with periodic acid to give formaldehyde (positive chromotropic acid test), and another aldehyde (IV), m.p.  $187^\circ$ ;  $[\alpha]_D + 11.6^\circ$  (C, 1.2);  $R_f$  0.9 in solvent A, 0.8 in D; mol. formula  $C_{29}H_{50}O$ ;  $\nu_{max}$  (KBr)  $1724\text{ cm}^{-1}$  (C=O); silver mirror with Tollens reagent;  $\delta$  (CDCl<sub>3</sub>): 9.7 (s, 1H of CHO), 2.34 p.p.m. (m, 2H of CH<sub>2</sub> next to keto).

A comparison of the mass spectra of methyl putrolate (II), its O-acetyl and oxo (IX) derivatives with methyl putranjivate showed the same base ion 205 besides many common ion peaks below mass ion 301. Hence putrolic acid could be related to putranjivic acid. This was established by LAH reduction of methyl O-tosyl putrolate (V) (see ref. 3 for similar hydrogenolysis of tosylate) when an alcohol (VI) m.p.,  $178^\circ$ ;  $[\alpha]_D + 4.2^\circ$  (C, 0.952);  $R_f$  0.40 in solvents A and D, 0.65 in E; mol. formula  $C_{30}H_{54}O$ , was obtained which was identical in mixed m.p., i.r. spectrum and t.l.c. with the alcohol obtained from methyl putranjivate (VIII) by catalytic hydrogenation followed by LAH reduction. Hence putrolic acid has structure (I) and the various transformations and relation to putranjivic acid (VIII) could be represented by structural formula.

Very recently, two publications<sup>4,5</sup> have appeared on investigation of the bark of the same tree. Sengupta *et al.*<sup>4</sup> isolated besides friedelin putranjivadiene and friedelanol, a new triterpenic ketone which was named roxburgholone and given the structure of 3  $\alpha$ -hydroxyfriedelan-7-one. They did not report any acid component. On the other hand, Garg



and Mitra<sup>5</sup> did isolate the acid which was named putranjic acid, and considered to be hydroxy triterpenic acid but not assigned any structure. The m.p. and spectral data of putranjic acid and its two derivatives are very close to those of putrolic acid and its derivatives but the molecular formulae differ. Garg and Mitra further reported the presence of an unidentified sterol, friedelin, putranjivadiene and putranjivanonol. The last compound seems to be the same as roxburgholone of Sengupta *et al.*<sup>4</sup>

1. Chopra, G. R., Jain, A. C. and Seshadri, T. R., *Curr. Sci.*, 1968 37, 301.
2. Bellamy, L. G., *The Infra-red Spectra of Complex Molecules*, Methuen & Co., London, 1958, p. 184.
3. Agarwal, K. P., Roy, A. C. and Dhar, M. L., *Ind. J. Chem.*, 1963, 1, 28.
4. Sengupta, P. and Mukherjee, J., *Tetrahedron*, 1968, 24, 6259.
5. Garg, H. S., and Mitra, C. R., *Phytochem.*, 1968, 7, 2053.

## MAGNETIC SYMMETRY AND ELASTIC COEFFICIENTS

T. S. G. KRISHNAMURTY AND P. GOPALAKRISHNAMURTY

Andhra University, Waltair

**E**LASTICITY expresses the relation between the applied stress and the resulting strain both of which are known to be represented by the second rank symmetric tensors. Bhagavantam and Suryanarayana<sup>1</sup> have enumerated the second and the third order elastic coefficients in respect of the 32 crystal classes employing the character method. Jahn<sup>2</sup> obtained identical results using the method of reduction of a representation. Krishnamurty<sup>3</sup> and Krishnamurty and Gopalakrishnamurty<sup>4</sup> have computed the number of non-vanishing independent fourth order elastic coefficients for the 32 classes of crystals. Since piezo-

magnetism is the appearance of a magnetic moment on the application of a stress (Bhagavantam<sup>5</sup>), one is led to investigate the connection between the two phenomena, namely piezomagnetism and elasticity, in crystals. This will be explained in what follows. Accordingly in this note the number of the second, the third and the fourth order elastic coefficients for each one of the 58 double-coloured magnetic point groups is derived on the basis of Jahn's<sup>2</sup> method.

If  $V$  denotes the representation of a polar vector and  $[V^2]$  represents the symmetrical product (Tisza<sup>6</sup>) of  $V$  with itself, the values