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

RECENTLY, four new triterpenes, viz., putrone, protrol, putranjivic acid and methyl putranjivate besides β-amyrin, its palmitate and stigmasterol were isolated by us from the leaves of *Putranjiva roxburghii* Wall. (N.O. Euphorbiaceae). 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 (0.06%; identity confirmed by comparison with authentic sample kindly supplied by Professor P.R. Jefferies), a mixture of triterpenic 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 that 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 CHCl₃-MeOH mixture as colourless crystals, m.p. 220–222°; [%] + 21° (C, 0.475); R, 0.6 in solvent B, 0.5 in F, 0.3 in G; ν max (nujol) 3500 (OH) and 1718 cm⁻¹ (C=O). The elemental analysis of this and its derivatives showed the mol. formula to be C₃₀H₵₂O₃. 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 CHCl₃-MeOH mixture as colourless long needles, m.p. 175–76°; [%] + 8.3° (C, 1.204); R, 0.4 in solvents A and D, and 0.8 in E; no colour with t.n.m.; ν max (KBr) 1730 cm⁻¹ (ester C=O); δ(CDCI₃): 3.90 p.p.m. (s, 3H of CO₂CH₃). Elemental analysis and mass spectrum determined its mol. formula as C₃₁H₵₄O₈ (M⁺ 474). The n.m.r. spectrum of methyl putrolate showed that it is a saturated molecule having 7–8 methyl groups (δ 0.84–1.28 p.p.m.) and a secondary alcohol (δ 4.2 p.p.m., multiplet of one proton of CHO). The presence of the alcoholic group was confirmed by preparing (i) methyl O-acetyl putrolate, m.p. 140–41°; [%] + 19° (C, 1.04); R, 0.3 in solvents A and D; M⁺ 516; mol. formula C₃₃H₶₀O₄; ν max (KBr) 1760 cm⁻¹; δ(CDCI₃): 2.18 (s, 3H of OCCO₂H), 3.79 (s, 3H of CO₂CH₃), 5.05 p.p.m. (m, 1H of CHOAc), and (ii) O-tosyl derivative, m.p. 141–42°; [%] − 27° (C, 1.09); R, 0.70 in solvent A and 0.75 in D; mol. formula C₃₅H₶₂O₅S₅. The secondary nature of the alcoholic group was shown by Jones’ oxidation of methyl putrolate to form methyl oxoputrolate, m.p. 152–54°; [%] + 24° (C, 1.0); R, 0.9 in solvent A and 0.8 in D; M⁺ 472; mol. formula C₃₃H₶₂O₅; ν max (nujol) 1757 cm⁻¹ (C=O); δ(CDCI₃): 3.82 (s, 3H of CO₂CH₃), 2.67 p.p.m. (m, 2H of CH₂ 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 CO₂H groups in putrolic acid show that it is a triterpenic seco-acid having four rings (I). That putrolic acid is an α-hydroxyacid is shown by the following facts. (i) The n.m.r. spectrum of methyl putrolate (II) shows no signals for α-methylene group in the region δ 2.8–2.5 p.p.m. (ii) The i.r. spectrum of methyl oxoputrolate showed only one carbonyl frequency which behaviour is reminiscent of α-keto esters. (iii) LAH reduction of methyl putrolate gives a 1,2-diol (III) (m.p. 212–14°; R, 0.1 in solvent A and 0.3 in C; mol. formula...
C\textsubscript{30}H\textsubscript{54}O\textsubscript{3} which undergoes cleavage with periodic acid to give formaldehyde (positive chromotropic acid test), and another aldehyde (IV), m.p. 187\textdegree; [\alpha]_b + 11.6\degree (C, 1.2); R, 0-9 in solvent A, 0-8 in D; mol. formula C\textsubscript{28}H\textsubscript{50}O; \nu\textsubscript{max.} (KBr) 1724 cm\textsuperscript{-1} (C=O); silver mirror with Tollens reagent; \delta (CDCl\textsubscript{3}) 9.7 (s, 1H of CHO), 2-34 p.p.m. (m, 2H of CH\textsubscript{2} 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 putronic 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\textdegree; [\alpha]_b + 4-2\degree (C, 0.952); R, 0-40 in solvents A and D, 0-65 in E; mol. formula C\textsubscript{30}H\textsubscript{54}O, was obtained which was identical in mixed m.p., i.r. spectrum and t.i.c. with the alcohol obtained from methyl putranjivate (VIII) by catalytic hydrogenation followed by LAH reduction. Hence putronic acid has structure (I) and the various transformations and relation to putranjivic acid (VIII) could be represented by structural formula.

Very recently, two publications\textsuperscript{4-5} have appeared on investigation of the bark of the same tree. Sengupta et al.\textsuperscript{4} isolated besides friedelin putranjivadione and friedelan, a new triterpenic ketone which was named roxburgholone and given the structure of 3\textsuperscript{a}-hydroxyfriedelan-7-one. They did not report any acid component. On the other hand, Garg and Mitra\textsuperscript{5} did isolate the acid which was named putranjivic acid, and considered to be hydroxy triterpenic acid but not assigned any structure. The m.p. and spectral data of putranjivic acid and its two derivatives are very close to those of putronic acid and its derivatives but the molecular formulæ differ. Garg and Mitra further reported the presence of an unidentified sterol, friedelin, putranjivadione and putranjivaronol. The last compound seems to be the same as roxburgholone of Sengupta et al.\textsuperscript{4}

MAGNETIC SYMMETRY AND ELASTIC COEFFICIENTS

T. S. G. KRISHNAMURTY AND P. GOPALAKRISHNAMURTY
Andhra University, Waltair

ELASTICITY 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\textsuperscript{1} have enumerated the second and the third order elastic coefficients in respect of the 32 crystal classes employing the character method. Jahn\textsuperscript{2} obtained identical results using the method of reduction of a representation. Krishnamurty\textsuperscript{3} and Krishnamurty and Gopalakrishnamurty\textsuperscript{4} 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\textsuperscript{5}), 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 method.

If \( V \) denotes the representation of a polar vector and \( [V]^2 \) represents the symmetrical product (Tisz\textsuperscript{6}) of \( V \) with itself, the values

---