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PUTRANJIVA ROXBURGHII WALL.—II.

TRITERPENES OF THE TRUNK BARK

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Abstract—Two new triterpenoids namely *putranjivanonol*, a hydroxy ketone, and *putranjic acid*, a hydroxy acid, have been isolated from the trunk bark of *Putranjiva roxburghii* Wall. (Euphorbiaceae) along with friedelin and putranjivadione and a sterol.

A CRYSTALLINE saponin, putranjivoside, m.p. 215–217°, $(\alpha)_D - 35°$ has been reported by us from the seed coat of *Putranjiva roxburghii* Wall. (Euphorbiaceae) and its constitution elucidated.[1] While continuing the work, the trunk bark of the tree yielded a few new triterpenoids, both neutral and acidic. The benzene-soluble neutral fraction of the alcoholic extractive of the bark, on chromatography over silica gel, yielded a sterol, m.p. 156–158°, friedelin, m.p. 264–268°, a triterpenoid diketone (I), a monohydroxy ketone (II), and the acidic fraction yielded a monohydroxy acid (III).

The diketone (I) ($C_{30}H_{48}O_2$, m.p. 282–284°, $(\alpha)_D - 26{\cdot}5°$) was found to be identical to the putranjivadione[2] (m.p. 284–289°, $(\alpha)_D - 36{\cdot}8$ recently reported from the whole plant presumably grown up to the shrub stage, which is identical with friedelan-3,7-dione as shown by chemical as well as mass spectral studies.

The more polar monohydroxy ketone (II), named putranjivanonol ($C_{30}H_{50}O_2$, m.p. 312–314°) gave a negative TNM test and showed the absence of any olefinic proton in its NMR spectra. Its i.r. spectra manifested prominent bands at 3448 cm^{-1} (hydroxyl group) and 1709 cm^{-1} (six-membered cyclic ketone). The NMR spectrum of putranjivanonol accounted for seven *tert* methyl groups at δ 1·18 (3H), 1·05 (3H), 0·98 (6H), 0·91 (6H) and 0·82 (3H) and a secondary methyl signal at δ 0·76 (3H). The presence of a methylene, adjacent to carbonyl, was observed as multiplet centred at δ 2·2 (2H) and a multiplet at δ 2·75 (1H) was accounted by one α-H to CO. On acetylation with pyridine and acetic anhydride it yielded a monoacetate, i.r. spectra of which showed absence of hydroxyl band and instead a new band at 1739 cm^{-1} (acetyl carbonyl) was observed along with a supporting band at 1250 cm^{-1}. The hydroxyl group in putranjivanonol is secondary as evident from the i.r. spectrum as well as the NMR spectra, the latter showing signals for eight methyl groups.

The carbonyl function in putranjivanonol was found to be chemically hindered as it did not yield any characteristic derivative. The degree of hindrance of the carbonyl could be compared to the C_7 ketone of putranjivadione as the former could not be reduced either by sodium borohydride or Huang Minlon modification of Wolff-Kishner reduction and as such the possibility of the ketone function being at C_3 is being ruled out in putranjivanonol.

[1] H. S. GARG and C. R. MITRA, *Planta Medica* **16**, 17 (1968).
[2] P. SEN GUPTA, A. K. CHAKRABORTY, A. M. DUFFIELD, L. J. DURHAM and C. DJERASSI, *Tetrahedron* **24**, 1205 (1968).

The new triterpenic acid (III) named putranjic acid ($C_{30}H_{50}O_3$, m.p. 218–220°, $(\alpha)_D$ 1°) also showed a negative TNM test and no absorption of olefinic proton in NMR spectrum of its methyl ester thereby suggesting it to be a saturated acid probably belonging to the friedelane series. The i.r. spectra of the acid showed the presence of a hydroxyl function (3448 cm^{-1}) and a carboxyl (1720 cm^{-1}) group. It gave a monoacetate, $C_{32}H_{52}O_4$, m.p. 197°; ν_{max} 3125 cm^{-1} (carboxyl OH) and 1718 cm^{-1} (acid CO), 1739 cm^{-1} (acetate carbonyl) with supporting band at 1250 cm^{-1}. With diazomethane in ether it yielded the monomethyl ester, methyl putranjate ,$C_{31}H_{52}O_3$, m.p. 176°; ν_{max} 3509 (hydroxyl) and 1724 cm^{-1} (ester carboxyl). The NMR spectra of Me-putranjate (in CCl_4) showed signals at δ 3·75 (3H, —COO CH_3), presence of seven methyl groups at δ 0·71 (3H), 0·85 (6H), 0·91 (3H), 0·98 (6H) and 1·01 (3H). The proton signal of $>CHOH$ at δ 4·05 for 1H was masked by the methyl ester signal, thus suggesting the hydroxyl in putranjic acid as secondary. The possibility of the location of the carboxyl group at C_{17} in putranjic acid was ruled out as methyl putranjate on alkaline hydrolysis (10 per cent; methanolic KOH) easily furnished putranjic acid. Me-putranjate on reduction with lithium aluminium hydride yielded a diol, $C_{30}H_{52}O_2$, m.p. 202°; ν_{max} 3433 cm^{-1} (OH) and no carbonyl absorption. The constitutive studies in both the compounds are being pursued.

EXPERIMENTAL

The melting points (uncorrected) were determined in open capillaries; the i.r. spectra were recorded in KBr, the NMR spectra in $CHCl_3$ and the rotations were measured in 1% $CHCl_3$ solution, unless otherwise stated.

The air-dried powdered bark (5 kg) was percolated with alcohol (4 l × 5) and the concentrated extract yielded a microcrystalline solid (30 g) which was separated into ether-soluble and ether-insoluble fractions. The ether-insoluble residue (20 g) on chromatography over silica gel (400 g) yielded the following compounds:

Putranjivadione. The crystallisate from hexane–benzene (1:3) eluate furnished putranjivadione (4·2 g), TLC single spot, m.p. 280–282°; $(\alpha)_D^{28}$ −26·5; ν_{max} 1709, 1460, 1428, 1388, 1379, 1361, 1342, 1290, 1245, 1227, 1212, 1170, 1099, 1081 and 1064 cm^{-1}; NMR δ 1·07, 1 00, 0 96, 0·88, 0·71 ppm; ORD α_{400} −115, α_{319} −1320, α_{310} −1075, α_{270} 1275, α_{222} 455. (Found: C, 81·04; H, 11·34. Calc. for $C_{30}H_{48}O_2$; C, 81 81; H, 10·90 per cent); identical to that recently reported.

Putranjivanonol. The benzene eluate yielded a triterpene hydroxy ketone (500 mg; TLC single spot), $C_{30}H_{50}O_2$, m.p. 312–314°; $(\alpha)_D^{35}$ −17 5; ν_{max} 3448, 1709, 1449, 1399, 1379, 1361, 1282, 1227, 1170, 1087, 1036, 1020, 1005, 980 and 862 cm^{-1}; NMR δ 2·75, 2·2, 1·18, 1·05, 0 98, 0·91, 0·82 and 0·76 ppm. (Found: C, 81·87; H, 11·69. $C_{30}H_{50}O_2$ required: C, 81·44; H, 11 31 per cent).

Putranjivanonol monoacetate. Putranjivanonol (100 mg) in pyridine (2 ml) was left overnight at room temperature with acetic anhydride (0·5 ml) and finally heated at 120–130° for 2 hr. The crude acetate was purified by chromatography (alumina 1:50, ether–hexane, 1:1) followed by crystallization from hexane–benzene (1:1), $C_{32}H_{52}O_3$, m.p. 321–323°; ν_{max} 1739, 1709 and 1250 cm^{-1}. (Found: C, 78·80; H, 11·31. $C_{32}H_{52}O_3$ required: C, 79 34; H, 10·79 per cent.)

Putranjic acid. The acidic component (2 4 g; $NaHCO_3$ soluble) of the ether-soluble fraction (*vide supra*) on chromatography over silica gel (hexane–benzene, 1:1) yielded colourless needles of a hydroxy acid, putranjic acid (850 mg), m p. 218–220°; $(\alpha)_D^{35°}$ 1·0°; ν_{max} 3448, 1724, 1460, 1389, 1361, 1227, 1099, 1053, 990 and 917 cm^{-1}. (Found: C, 78 01; H, 11·24. $C_{30}H_{50}O_3$ required: C, 78·60; H, 10 91 per cent.)

Putranjic acid monoacetate Putranjic acid (150 mg) in pyridine (2 ml) was refluxed with acetic anhydride (0·5 ml) at 120–130° (2 hr). The crude product was crystallized from benzene, $C_{32}H_{52}O_4$, m.p. 196°; $(\alpha)_D^{35°}$ −1·5°; ν_{max} 3125, 1739, 1724 and 1250 cm^{-1}. (Found: C, 76 80; H, 11·04. $C_{32}H_{52}O_4$ required: C, 76·80; H, 10·40 per cent)

Methyl putranjate. To putranjic acid (250 mg) in ether (10 ml) was added CH_2N_2 in ether and the reaction mixture left overnight; the residue, on chromatography over alumina (hexane–benzene, 1:1), yielded silky needles of methyl putranjate, $C_{31}H_{52}O_3$, m p. 176°; $(\alpha)_D^{35}$ −23·5°; ν_{max} 3471, 1724, 1460, 1389, 1370, 1258 cm^{-1}; NMR in CCl_4: δ 3·75, 1·01, 0 98, 0 91, 0·85 and 0·71 ppm. (Found: C, 78 08, H, 11·49. $C_{31}H_{52}O_3$ required: C, 78 81; H, 11·02 per cent.)

$LiAlH_4$ *reduction of methyl putranjate.* Methyl putranjate (150 mg) in tetrahydrofuran (5 ml) was stirred at room temperature for 8 hr with $LiAlH_4$ (250 mg in 5 ml tetrahydrofuran), poured onto crushed ice, acidified (5% H_2SO_4), extracted with ether, and after usual processing and chromatography (alumina, 1:50;

hexane–benzene, 1:2) yielded the diol, $C_{30}H_{52}O_2$, m.p. 202°; ν_{max} 3450, 1460, 1309, 1361, 1087 and 1075 cm^{-1}. (Found: C, 80·63; H, 12·27. $C_{30}H_{52}O_2$ required: C, 81·08; H, 11·71 per cent.)

Alkaline hydrolysis of methyl putranjate. Methyl putranjate (100 mg) was refluxed with methanolic KOH (10%) for 1 hr and the solvent removed under reduced pressure. The gelatinous salt was acidified (5% H_2SO_4), extracted with ether and chromatography over silica gel (hexane–benzene, 1:1) followed by crystallization (benzene) yielded putranjic acid, m.p. and m.m.p. 218–220°; superimposable i.r. spectra with that of the parent acid.

Sterol. The L-B positive residue (450 mg) from hexane eluate on crystallization (alcohol) melted at 156–158°.

Friedelin. The residue from hexane–benzene (1:1) eluate on crystallization from benzene yielded friedelin (850 mg), m.p. 264–268°; $(\alpha)_D^{28}$ −30°; identified by m.m.p. and superimposable i.r. spectra with that of an authentic sample.

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