Department for facilities, and to Dr. K. V. Ramanathan, Sophisticated Instruments Facility, I.I.Sc., Bangalore, for recording ^{13}C nmr spectra on a Bruker WH-270 spectrometer.

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Chemical Examination of Pods of *Cassia roxburghii*

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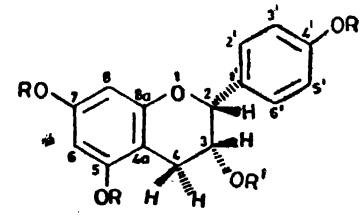
Manuscript received 12 December 1989, revised 18 April 1990, accepted 3 July 1990

EARLIER, we communicated the isolation and structural elucidation of roxburghinol[1], a new 1,2-dihydroanthraquinone and roxburghin[2], a new tetrahydroxystilbene from the leaves and wood of the *Cassia roxburghii* Benth. respectively. In the present communication, the results of chemical examination of pods of this plant is reported.

The air-dried and powdered pods of *C. roxburghii* were extracted with methanol. The solvent-free residue was separated into petroleum ether solubles and insolubles. The petroleum ether solubles on column chromatographic separation (silica gel) led to the isolation of two compounds, designated as compounds A and B.

Compound-A (0.002%), m.p. 138°, $[\alpha]_D$ −36°, $C_{29}H_{50}O$, M^+ 414, gave positive Liebermann-Burchardt test[3] for sterols and was characterised as β-sitosterol[4] by direct comparison with an authentic sample. Compound-B. crystallised from chloroform as orange flakes (0.0015%), m.p. 196°, $C_{15}H_{10}O_4$, M^+ 254, gave pink colour with alcoholic magnesium acetate indicating it to be a hydroxy-anthraquinone[5]. From the spectral data (ir, uv, ^1H nmr, mass) and also by a direct comparison, it was identified as 1,8-dihydroxy-3-methylanthraquinone (chrysophanol)[2].

The petroleum ether insoluble fraction, after the usual work up, followed by column chromatography (silica gel), yielded three compounds, designated as compounds C, D and E. Compound-C crystallised from $CHCl_3$-acetone (9 ; 1, v/v) as cream coloured fluffy solid (0.002%), m.p. 224°, $C_{14}H_{12}O_4$, M^+ 214, formed tetraacetate and tetramethyl ether. From the analytical and spectral data (ir, uv, ^1H nmr, ^{13}C nmr and mass) it was identified as roxburghin[2], which was confirmed by a direct comparison with an authentic sample. Compound-D crystallised from methanol as colourless needles (0.003%), m.p. 140–42°, $C_{10}H_{10}O_4$, M^+ 194, did not give any colour tests, and was characterised as terephthalic acid[6] by its spectral data and also by direct comparison with an authentic sample.



1 ; R=R′=H
2 ; R=R′=Ac
3 ; R=CH_3, R′=H

Compound-E (1) crystallised from chloroform as light cream coloured flakes (0.01%), m p. 242°, $[\alpha]_D$ −56 66°, $C_{15}H_{14}O_5$, M^+ 274, gave characteristic colour reactions of flavan-3-ols[7]. It formed a tetraacetate (2), m.p. 127°, $C_{23}H_{22}O_9$, M^+ 442 and a trimethyl ether (3), m p. 110°, $C_{18}H_{20}O_5$, M^+ 316, indicating the presence of three phenolic hydroxyls and one alcoholic hydroxyl group. The ir spectrum (KBr) of 1 showed characteristic bands at 3 300–3 500br (OH), 2 900 (aliphatic CH), 1 500-1 600 cm^{-1} (aromatic C=C). Its uv spectrum, λ_{max} (MeOH) (log ε) 228sh (4.71) and 270 nm (4.12) was similar to those of flavan-3-ols[8]. The overall signal pattern of compound-E in its ^1H nmr spectrum (100 MHz, DMSO-d_6) bears resemblences to that of flavan-3-ols[9], δ 2.88 (2H, m, H-4α, H-4β), 3.2 (1H, m, D_2O exchangeable, C_3-OH , 4.2 (1H, m, H-3), 4.87 (1H, d, *J* 1.7 Hz, H-2), 5.96 (1H, d, *J* 2.5 Hz, H-6), 6.05 (1H, d, *J* 2.5 Hz, H-8), 6.75 (2H, d, *J* 8.5 Hz, H-3′ and H-5′), 7.27 (2H, d, *J* 8.5 Hz, H-2′ and H-6′), 8.46 (1H, s, D_2O exchangeable, C_5-OH), 8.57 (1H, s, D_2O exchangeable, C_7-OH) and 8.79 (1H, s, D_2O exchangeable, C_4'-OH). Hence compound-E was characterised as 4′,5,7-trihydroxy-flavan-3-ol. The mass spectrum of 1 showed prominent ions at *m/z* 274 $[M]^+$ (100), 256 $[M-H_2O]$ (10), 136 (RDA fragment) (40) and 139 (RDA fragment with proton shift) (97) supporting the assigned structure[10]. The compound showed negative Cotton effect in its C.D. spectrum. The sign and magnitude is almost identical to that of (−) epiafzelechin[11]. Thus compound-E was characterised as (−)epiafzelechin, which was confirmed by direct comparison with an authentic sample.

The ^{13}C nmr spectrum (39.2 MHz, DMSO-d_6) of 1 showed the appropriate signals for 12 chemically different carbon atoms. The peak positions

and splitting pattern of these signals in the off resonance decoupled spectrum are characteristic of flavan-3-ols[12] ; δ 156.47 (s, C-5), 156.20 (s, C-4′ and -7), 153.72 (s, C-8a), 129.93 (s, C-1′), 128.19 (d, C-2′ and -6′), 114.37 (d, C-3′ and -5′), 98.39 (s, C-4a), 95.09 (d, C-6), 94.06 (d, C-8), 78.02 (d, C-2), 64.80 (d, C-3) and 28.30 (t, C-4). This is the first report of ^{13}C nmr of (−)epiafzelechin.

Acknowledgement

One of the authors (S. P. R.) is grateful to U.G.C., New Delhi, for the award of a Teacher Fellowship.

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Phytochemical Examination of *Spilanthus acemella* (Murr.)

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Manuscript received 19 March 1990, revised 29 June 1990, accepted 3 July 1990

IN consideration of various medicinal properties[1] and various reports[2] on *Spilanthus acemella* Murr. (Fam. : Compositae) we undertook further investigation on the plant. In the present communication we report some of our results.

The air-dried whole plant of *S. acemella* was extracted successively with petroleum ether and ethanol. The petroleum ether extract on chromatography (silica gel) and elution with petroleum ether-benzene (9 : 1) furnished colourless crystalline needles, m.p. 86° ; ν_{max} (KBr) 3 425 (OH) and 1 050 cm^{-1} (C – O) which was identified as myricyl alcohol (1), (m m.p., co-tlc and co-ir). Its acetate melted at 72°. The petroleum ether-benzene (4 : 1) eluent gave colourless shining flakes soluble in $NaHCO_3$, m.p. 59° ; ν_{max} (KBr) 1 730 cm^{-1} (acid C=O) which was identified as palmitic acid (2) by usual comparison (m m.p., co-tlc, co-ir). Elution of the column with petroleum ether-benzene (2 : 1) gave white flakes, soluble in $NaHCO_3$, m.p. 69° ; ν_{max} (KBr) 1 730 cm^{-1} (acid C=O) and which was identified as stearic acid (3) from its ^1H nmr spectrum and usual comparison (m.m.p., co-tlc, co-ir). The petroleum ether-benzene (1 : 1) eluent gave a solid, m.p. 223 – 25° ; ν_{max} (KBr) 1 732 cm^{-1} (ester C=O), positive to Salkowski's reaction for triterpenoids. Hydrolysis of the compound gave a solid, m.p. 181 – 83°, identical with α-amyrin. So the compound was identified was α-amyrin acetate (4).

The petroleum ether-benzene (1 : 2) eluent gave β-sitosterol (5) m.p 137°, identified from its ^1H nmr and mass spectra and by usual comparison (m.m p., co-tlc and co-ir). The benzene eluent gave a solid, m.p. 148 – 50°, which was identified as β-amyrin (6) which was identified from its ^1H nmr spectra and its acetate and also by usual comparison (m.m.p., co-tlc, co-ir).

Elution of column with benzene-ethyl acetate (9 : 1) gave a solid, m.p. 182°, which was found to be identical to the hydrolysis product of 4, and was identified as α-amyrin (7).

The concentrated ethanol extract was extracted with ether. The residue obtained on evaporation of ether was repeatedly crystallised with $CHCl_3$-C_2H_5OH (1 : 1) to white crystals, m.p. 302 – 03°d, $[\alpha]_D$ – 38° (pyridine), positive to Molisch's test for sugars. It was found to be a phytosterolin and the mass spectrum of the compound indicated it to be a mixture of β-sitosterol-D(+)-glucoside and stigmasterol-D(+)-glucoside.

Acknowledgement

Thanks are due to Dr. D. S. Bhakuni, Deputy Director, C.D.R.I., Lucknow, for spectral measurements and elemental analyses. Thanks are also due to I.C.M.R., New Delhi, for financial assistance.

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