Chemical Constituents of the Roots of *Millingtonia hortensis* Linn. and *Acacia nilotica* (Linn.) Del.

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MILLINGTONIA hortensis Linn. (Bignoniaceae) commonly known as 'Akash Neem' or 'Neem Chameli' is a well known plant. The perusal of literature revealed that the stem of this plant has been investigated by Joshi *et al*[1]. The present work deals with the isolation and characterization of various chemical constituents from the root.

Acacia nilotica (Linn.) Del. (Leguminosae) is an important medicinal plant[2] and used as an anthelmintic, and in bronchitis, diarrhoea, etc[3,4]. Some work has been reported on stem[5], so we undertook a systematic chemical investigation of the bark and heartwood of root.

Experimental

Chemical Constituents from Millingtonia hortensis *Linn. :*

Air-dried coarsely powdered root (4.5 kg) was extracted thrice with hot petroleum-ether (60-80°). The concentrated extract was chromatographed over silica-gel. Elution with solvents of increasing polarity gave the following compounds.

Hentriacontane :

The petroleum ether eluate afforded hentriacontane, crystallized from ethyl acetate as colourless crystals, m.p. 68° ; negative TNM test ; M^+ 436 ; IR ν_{max} (KBr) 1460 and a doublet at 730-720 cm^{-1} ; identical (mmp, TLC) with an authentic sample.

Lapachol :

Elution of the column with pet. ether–benzene (3 : 1) afforded lapachol, m.p. 138-39° (benzene) ; violet red colour with ferric chloride and deep red solution was obtained with aqueous sodium hydroxide ; UV λ_{max} (EtOH) 251, 276, 329 nm ; IR ν_{max} (KBr) 3335, 1660, 1637, 1591 cm^{-1} ; identical (mmp, TLC & IR) with an authentic sample.

Hentriacontanol-1 :

Further elution of the column with pet. ether-benzene (1 : 1) yielded white crystalline, m.p. 84° (MeOH) ; negative TNM test ; M^+.452 ; IR ν_{max} (KBr) 3280, 1470 and a doublet at 730-720 cm^{-1} etc., ; Acetate (Ac_2O/Pyr.), m.p. 69-70° ; identical (mmp, TLC) with an authentic sample.

β-sitosterol :

Elution of the column with pet. ether-benzene (1 : 3) gave β-sitosterol, shining needles, m.p. 136-37° ($CHCl_3$/MeOH) gave positive Liebermann-Burchard test for sterol ; IR ν_{max} (KBr) 3400, 1050, 800, 715 cm^{-1}, etc. ; Acetate (Ac_2O/Pyr.), m.p. 125-26° ; Benzoate (C_6H_5COCl/Pyr.), m.p. 143-4° ; identical (mmp, TLC & IR) with an authentic sample.

Paulownin :

Further elution of the column with benzene-ethyl-acetate (3 : 1) gave paulownin, m.p. 104° (benzene) ; Positive Labat and Hansen tests ; Negative to TNM and $FeCl_3$ tests ; IR ν_{max} (KBr) 3400, 1610, 1265, 970, 780 cm^{-1}, etc. ; Acetate (Ac_2O/Pyr.), m.p. 143° ; identical (mmp, TLC & IR) with an authentic sample.

Chemical Constituents from Acacia nilotica *(Linn.) Del. Root Bark :* Completely dried and coarsely powdered root-bark was exhaustively extracted with benzene. The concentrated benzene extract fractionated into soluble and insoluble petroleum ether fractions. The soluble portion was chromatographed over silica-gel, elution being made with solvents of increasing polarity and the following compounds were obtained :

Octacosanol : Elution of the column with pet. ether-benzene (3 : 1) furnished octacosanol, white crystalline compound, m.p. 83° (Pet. ether) ; No colour with TNM ; IR ν_{max} (KBr) 3360, 2960, 2820, 1460, 1050, 730 and 720 cm^{-1} ; Acetate (Ac_2O/Pyr.), m.p. 64° ; identical (mmp, TLC & IR) with an authentic sample.

β-amyrin : Further elution of the column with pet. ether-benzene (1 : 1) yielded β-amyrin, m.p. 196-97° (EtOH) ; yellow colour with TNM ; Positive Liebermann-Burchard and Noller's test ; IR ν_{max} (KBr) 3360, 2960, 2880, 1650, 1465, 1040, 890 cm^{-1} ; Acetate (Ac_2O/Pyr.), m.p. 238° ; Benzoate (C_6H_5COCl/Pyr,) m.p. 228° ; identical (mmp, TLC & IR) with an authentic sample.

β-sitosterol : Further elution of the column with pet. ether-benzene (1 : 3) furnished β-sitosterol, m.p. 136° ($CHCl_3$/MeOH) ; Acetate (Ac_2O/Pyr.), m.p. 125-26° identical (mmp, TLC & IR) with an authentic sample.

Betulin : Elution of the column with benzene-ethylacetate (3 : 1) yielded betulin, white shining needles, m.p. 248-49° (EtOH) ; M^+ 442 ; Positive Liebermann-Burchard test and Noller's test ; Yellow colour with TNM ; IR ν_{max} (KBr) 3390, 2960, 1650, 1460, 1370 cm^{-1} etc. ; Acetate (Ac_2O/Pyr.), m.p. 215-16° ; identical (mmp, TLC & IR) with an authentic sample.

Root-heartwood : Dried chipps of heartwood was extracted with hot petroleum ether (60-80°). The concentrated extract when chromatographed over silica-gel gave β-amyrin and β-sitosterol only.

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References

1. K. C. JOSHI, L. PRAKASH and P. SINGH, *J. Indian Chem. Soc.*, 1973, **50**, 561.
2. R. N. CHOPRA *et al* ; "Wealth of India, Raw Materials", CSIR, New Delhi, 1948, Vol. 1, p. 5.
3. K. R. KIRTIKAR and B. D. BASU, "Indian Medicinal Plants", 1975, Vol. 3, p. 1947.
4. R. N. CHOPRA, S. L. NAYAR and I. C. CHOPRA, Glossary of Indian Medicinal Plants, CSIR, New Delhi, 1956, p. 2.
5. H. I. ELSISSI, A. A. EL SISSI, M. S. ISHAK and A. A. SHERBIENV, *Leder*, 1967, **18**, 32.

Chemical Constituents of *Dillenia indica* Linn. and *Vitex negundo* Linn.

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DILLENIA indica Linn[1]. *(Dilleniaceae)* commonly known as "Chalta" is a large evergreen tree occurring throughout India and the alcoholic extract of its leaves was found to cause depression of central nervous system[2]. Literature survey revealed that some work has been done on the stem bark[3] and fruits[4] of this plant. We now report the results of chemical examination of the leaves of this plant on which no work has been done so far.

Vitex negundo Linn. *(Verbenaceae)* is reported to have medicinal importance[5]. Its roots used as expectorant and febrifuge while the leaves are applied in the removal of foetid discharges and in rheumatic pains of joints. The leaves and seeds of this plant have been investigated earlier[6-12]. A chemical investigation of the root of the plant has, therefore, been undertaken.

D. indica : The air dried powdered leaves were successively extracted with petroleum ether (60-80°) and chloroform. The petroleum ether (60-80°) extract was concentrated and separated into acidic and neutral fractions after following usual procedure.

Experimental

The acidic fraction was esterified with CH_2N_2 and the product on chromatography over silica gel furnished a solid m.p. 216°, identified as methyl betulinate (m.m.p. and CO – IR).

The neutral fraction was subjected to chromatographic separation over silica gel. Elution of the column with petroleum ether (60-80°) and benzene (1 : 1) mixture afforded a solid crystallised from methanol in shining flakes, m.p. 108°, ν_{max}^{KBr} 1700 cm^{-1} (carbonyl), oxime, m.p. 170° ; NMR in $CDCl_3$ (δ) 0.65, 2H, bs (cyclopropyl methylene), four singlets of 3 protons each at 0.85, 0.95, 1.00 and 1.01 (for tert. $-\overset{|}{C}-CH_3$) ; 1.21, 3H, d (J = 6 cps) ($-CH-CH_3$) ; 1.65, 3H, s, 1.70, 3H, s for the vinylic methyls and 5.15, 1H, m (olefinic proton).

The mass spectrum of the compound exhibits, a close resemblance to cycloartenone[14] showing significant peaks at m/e 424 (M^+), 409, 340, 313 and 286. Finally this compound was identified as cycloartenone by usual comparison (m.m.p., CO – TLC and superimposable IR spectra) with authentic sample.

Further elution of the column with the same solvent furnished two compounds : one having m.p. 88°, ν_{max}^{KBr} 3300 cm^{-1}, MS : 452 (M^+), 434, 421 and another compound, m.p. 137°, the m.p. of its acetate is 127-8°. These two compounds were identified as *n*-hentriacontanol and β-sitosterol respectively by comparative studies (m.m.p., Co – TLC and CO – IR) with the authentic samples.

The fraction eluted with benzene-chloroform (1 : 1) yielded a triterpene crystallised from methanol, m.p. 252°, ν_{max}^{KBr} 3480 cm^{-1}, acetate, m.p. 217°, identified as betulin by usual comparison (m.m.p., Co – TLC and CO – IR).

The chloroform extract on usual chromatography over silica gel yielded β-sitosterol and betulinic acid.

V. negundo : The dried and powdered root was successively extracted with petroleum ether (60-80°) and benzene. The petroleum ether (60-80°) extract was chromatographed over Brockmann alumina. Elution of the column with petroleum ether (60-80°) gave a solid which on repeated crystallisation from petroleum ether furnished colourless needles, m.p. 68°. It does not respond to Liebermann-Burchardt test for sterol or triterpene. The IR spectrum of this compound shows absorption peaks at 2920 and 2850 (C – H stretching), 1465, 1460, 1370 ($-\overset{|}{C}-CH_3$ bending), 730, 720 cm^{-1} [$(CH_2)_n$ bending]. The NMR spectrum (100 MHz, $CDCl_3$) showed signals