PART - IV

CHEMICAL INVESTIGATION ON INDIAN PLANTS

PART - IV

Chemical investigation on some Indian Plants :

Chemical investigation on the following Plants was undertaken and the results are shown in the attached REPRINT NO.1 and REPRINT NO.2.

REPRINT NO. 1 :

1. Cyathea spinulosa Wall (Filices)
2. Antidesma diandrum Roth (Euphorbiaceae)
3. Euphorbia jacuemontii Boiss (Euphorbiaceae)
4. Gelonium bifarium Roxb (Euphorbiaceae)
5. Soyamida febrifuga A.Juss (Meliaceae)

REPRINT NO. 2 :

1. Fluggea microcarpa Blume (Euphorbiaceae)
2. Sapium baccatum Roxb (Euphoroiaceae)
3. Skimmia wallichii (Rutaceae)

REPRINT NO. 1

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identity in absolute configuration was established by CD comparison—$\Delta\epsilon_{196}$ +7·2 from either source. The NMR spectrum of the isolated calamenene showed it to be the *cis*-isomer[8] essentially free of diastereomeric material. The negative ^1L_b band ($\Delta\epsilon_{278}=-0{\cdot}25$) suggests structure II.[8]

Acknowledgement—The work at U.W. was supported by NIH Grant GM-18143.

[8] ANDERSEN, N. H., SYRDAL, D. D. and GRAHAM, C. (1972) *Tetrahedron Letters* 905.

Phytochemistry, 1973, Vol. 12, pp. 1819 to 1820. Pergamon Press. Printed in England.

FILICES, etc.

PHYTOSTEROLS IN PLANTS

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Key Word Index—*Cyathea spinulosa*; Filices; Fern; lupeol; *Antidesma diandra*; *Euphorbia jacquemontii*; *Gelonium bifarium*; Euphorbiaceae; Angiospermae taraxerone; sitosterol; epimultiflorenol; multiflorenol; bauerenol; *Soymida febrifuga*; Meliaceae; methyl angolensate; sitosterol.

Plant. Cyathea spinulosa Wall[1] (Syn. *Hemitelia decipines* J. Scott). Filices. *Occurrence.* Middle and upper hill forest, rarely found near Kalimpong and Darjeeling, India. *Previous work.* None.

Isolation and identification. The powdered whole plant was extracted with C_6H_6 and the neutral fraction gave *lupeol*,[2] m.p. 214–215°, $[\alpha]_D$ +26·4°, its acetate m.p. 216–217°, $[\alpha]_D$ +47·5° confirmed by m.m.p., IR and co-TLC with an authentic sample. The second solid has been identified as *sitosterol.*

Plant. Antidesma diandrum Roth.[3] Euphorbiaceae. *Occurrence.* Tropical Himalaya, from Garwhal eastwards and southwards to Travancore, India.

Isolation and identification. The powdered trunk was extracted with benzene and the neutral part afforded *sitosterol.*

Plant. Euphorbia jacquemontii Boiss; Euphorbiaceae.[4] *Occurrence.* Throughout the Western Himalayan region of India. *Previous work.* None.

Isolation and identification. The powdered trunk bark was extracted with C_6H_6 and the neutral part on chromatography first gave *taraxerone*, $C_{30}H_{50}O$,* m.p. 238–240°, $[\alpha]_D$ 10·8°[5] confirmed by IR, NMR and co-TLC with authentic specimen and by conversion to

* Satisfactory analysis, $[\alpha]_D$ in $CHCl_3$, 60 Mc NMR in $CDCl_3$ with TMS as internal standard.

[1] COWAN, A. M. and COWAN, J. M. (1929) *The Trees of Northern Bengal*, p. 143, Bengal Secretariat Book Depot, Calcutta.
[2] HALSALL, T. G., JONES, E. R. H. and MEAKINS, G. D. (1952) *J. Chem. Soc.* 2862.
[3] HOOKER, J. D. (1954) *Flora of British India*, Vol. 5, p. 361, Reeve, London.
[4] HOOKER, J. D. (1954) *Flora of British India*, p. 238, Reeve, London.
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taraxerol, m.p. 278–280°, $[\alpha]_D$ +3·7°, acetate, m.p. 295–297°, $[\alpha]_D$ +9·16°. The second solid was an alcohol, $C_{23}H_{48}O$, m.p. 87–88°, $[\alpha]_D$ −22·42° (IR: 3275 cm^{-1}); acetate, $C_{25}H_{50}O_2$, m.p. 70–71° (IR: 1725 and 1245 cm^{-1}) but could not be identified for want of sufficient material. The last solid *sitosterol*, $C_{29}H_{50}O$, m.p. 137–138°, $[\alpha]_D$ −36° confirmed by m.m.p., IR and co-TLC with authentic specimen. Acetate, m.p. 127°, $[\alpha]_D$ −4°.

Plant. Gelonium bifarium Roxb;[6] Euphorbiaceae. *Occurrence.* Andaman islands, Malay islands. *Previous work.* Other sister species.[7,8]

Isolation and identification. The powdered trunk bark was extracted with C_6H_6. The neutral part gave a complex mixture of crystalline substances which on acetylation afforded a mixture of at least 3 acetates (TLC). On fractional crystallization it first afforded bauerenol acetate, $C_{32}H_{52}O_2$, m.p. 282–284°, $[\alpha]_D$ 0°, hydrolysis of which gave *bauerenol*, $C_{30}H_{50}O$, m.p. 208–209°, $[\alpha]_D$ −20° confirmed by m.m.p., IR and co-TLC with authentic specimen. From the mother liquor two other solids were separated by fractional crystallization. The first solid multiflorenol acetate $C_{32}H_{52}O_2$, m.p. 220–222°, $[\alpha]_D$ 0° and its corresponding alcohol, *multiflorenol*, $C_{30}H_{50}O$, m.p. 188–190°, $[\alpha]_D$ −30° confirmed by m.m.p. and IR comparison with authentic specimen. The third solid isolated from the mother liquor has been identified as epimultiflorenol acetate, $C_{32}H_{52}O_2$, m.p. 220–222°, $[\alpha]_D$ 0° and its corresponding alcohol *epi*multiflorenol, m.p. 206–208°, $[\alpha]_D$ 0° and its identity has been confirmed by preparing the alcohol from multiflorenone by the method of Paton *et al.*[9] The last solid m.p. 135–137° has been identified as *sitosterol.*

Plant. Soymida febrifuga A. Juss.[10] Meliaceae. *Occurrence.* Dry forests of Western Peninsula, extending northwards to Marwara, the Mirzapur Hill and Chot Nagpur of India. *Medicinal use.* Bark, astringent, bitter tonic, febrifuge, used in general debility, intermittent fevers, diarrhoea and dysentry. *Previous work.* bitter substances from bark.[11]

Isolation and identification. The powdered trunk bark was extracted with C_6H_6 and the chromatography of the neutral part over alumina first afforded *sitosterol*, m.p. 137–138°, $[\alpha]_D$ −36° confirmed by m.m.p. and IR comparison with authentic specimen. The second solid, m.p. 202–204°, $[\alpha]_D$ −42° coming out in C_6H_6–petrol. (4:1) showed in the NMR spectrum the presence of two α (δ 7·37) and one β-furanic protons (δ 6·35), the H-17 proton (δ 5·62) α-to the furan ring, two vinyl proton singlet $\sim$ δ5·00, characteristic of the vinylidene group exocyclic to a cyclohexane ring, two doublets (J 14 Hz) each one proton, assignable to the isolated geminal protons at C-15 and five three proton singlet assignable to one methyl ester and for quaternary methyls. All the above spectral data are in accord with *methyl angolensate*[12] and the compound has been found to be identical with the same confirmed by m.m.p. IR, co-TLC and NMR spectra with an authentic specimen.

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REPRINT NO. 2

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Printed in England.

PHYTOCHEMICAL REPORTS
PHYTOSTEROLS IN EUPHORBIACEAE AND RUTACEAE*

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(Received 19 March 1974)

Key Word Index - Fluggea microcarpa; Euphorbiaceae; hexacosane; fiedelin; friedelanol; sitosterol; Sapium baccatum; Euphorbiaceae; acetoxy aleuritolic acid; Skimmia wallichii; Rutaceae; taraxerone; 3-epitaraxerol; taraxerol; sitosterol.

Plant. Fluggea microcarpa Blume [2,3] (Syn Flueggea microcarpa Blume); Euphorbiaceae. Occurrence. Throughout India; from Kashmir ascending the Himalaya to 5000 ft. to Bhutan, and Assam and southwards to Malacca and Travancore. Uses. Medicinal [4]. Previous work [5]. Bergenin and isocoumarin in leaves.

Isolation and identification. The powdered trunk bark was extracted with C_6H_6 and the neutral fraction on chromatography over deactivated alumina afforded several crystalline solids: hexacosane, mp 58-59°; fiedelin mp 259-261°, $[\alpha]_D$ - 32°, ν_{max} 1708 cm^{-1} (six-membered ring ketone), oxime, mp 293-295°, $[\alpha]_D$ + 54.6°, friedelanol, mp 296-298°, $[\alpha]_D$ + 15.5°, acetate, mp 314-316°, and sitosterol, mp 136-137°, $[\alpha]_D$ - 34°, acetate, mp 127-129°, $[\alpha]_D$ - 39°. The identity of the above compounds was confirmed by mmp IR and co - TLC with authentic samples.

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* Part II of a series on Plant Phytosterols; for Part I see Ref. / 1 /.

Plant. Saplum-baccatum Roxb; [6] Euphorbiaceae. Occurrence. Assam, Sylhet and Khasia Mountains, India. Previous work. [7-10] Isolation and characterization of taraxerone, taraxerol, sitosterol, 1-hexacosanol, 3-3'-di-O-methyl ellagic acid [11].

Isolation and identification. The acidic fraction from the C_6H_6 extract of the stem and trunk bark of the plant on esterfication with CH_2N_2 followed by chromatography furnished a crystalline solid, mp 241-243°, $[\alpha]_D$ + 21.8°, no UV absorption above 220 nm, $\nu_{max}^{CHCl_3}$ 1738 cm^{-1} (broad, -OCOMe and COOMe), 1245 cm^{-1} (-OCOMe), NMR signals at δ 5.45 (1H, vinyl proton, trisubstituted double bond), δ 4.42 (1H, H-C-O-COMe), δ 2.05 (3H, -OCOMe), δ 3.54 (3H, -COOMe) and several sharp signals between δ 0.8 to 1.55 (21H, seven methyl groups). Hydrolysis of the ester with 5% methanolic KOH yielded an alcohol, mp 208-210°, $[\alpha]_D$ + 15.6°, $\nu_{max}^{CHCl_3}$ 3490 cm^{-1} (-OH), 1738 cm^{-1} (-COOMe). Oxidation of alcohol by CrO_3-C_6H_5N complex furnished a ketone, mp 174-176°, $[\alpha]_D$ + 14.2°, ν_{max}^{KBr} 1708 cm^{-1} (C=O), 1738 cm^{-1} (-COOMe). The acid obtained from the plant is therefore acetoxy aleuritolic acid, the physical data on the ester, alcohol and ketone being strikingly similar to those obtained for the known compound [12].

Plant. Skimmia wallichii Hk [13]; Rutaceae. Occurrence. A small procumbent shrub about 4ft. high, fairly common in Singalila Range, from 9000-11000 ft. Previous work. None. Isolation and identification. The powdered bark of the plant was extracted with C_6H_6 and the neutral fraction on chromatography over deactivated alumina first gave four crystalline compounds; the first mp 238-239°, $[\alpha]_D$ + 11°, ν_{max} 1710 cm^{-1} (six meambered ring ketone) was identical with taraxerone

(mmp and IR); 3-epitaraxerol [14] mp 261-263°, $[\alpha]_D$ - 25.6°, ν_{max} 3420 cm^{-1}(-OH) and 825 cm^{-1}(trisubstituted double bond), acetate, mp 160-162°, $[\alpha]_D$ -43°. Oxidation of the alcohol by CrO_3 -C_6H_5N complex-furnished taraxerone. The alcohol, 3-epitaraxerol and its oxidised product, taraxerone were identified by mmp, IR and co-TLC; taraxerol, mp 272-274°, $[\alpha]_D$ + 5.5°, acetate, mp 295-297°, $[\alpha]_D$ + 10° confirmed by mmp, IR and co-TLC with an authentic sample; and sitosterol (mmp and IR).

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REPRINT NO. 3

For Convention of Chemists 1974 : Section : Organic Chemistry.

TRITERPENES FROM POLYPODIUM JUGLANDIFOLIUM

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ABSTRACT

The neutral portion of the benzene extract of the rhizomes of Polypodium juglandifolium on chromatography afforded, from the least polar-fraction, two hydrocarbons-Fernene, $C_{30}H_{50}$, m.p. 169-70°, $(\alpha)_D$ - 16.3° and Filicene, $C_{30}H_{50}$, m.p. 231-32° (lit. 288.5-229.5°, Ref : H. Ageta, K. Iwata and S. Natori, Tetrahedron Letters, No. 46, pp 3413-3418, 1964), $(\alpha)_D$ + 49.6° identical with the authentic specimens (m.m.p and IR). The next fraction obtained from the chromatography m.p. 121-2° has been found to be a mixture of cycloläudenol, $C_{31}H_{52}O$, m.p. 122-23° and a new C-32 triterpene alcohol $C_{32}H_{54}O$. The new triterpene alcohol $C_{32}H_{54}O$ has established as having cycloläudenol nucleus with the extra carbon in the side chain from mass spectrometric studies of the original mixture, its acetate and the dihydroderivative and the acetate of the dihydro compound. The position of the double bond in the side chain has been tentatively assigned at 25 (26) also from mass spectrometric fragmentation pattern. Further work is in progress to locate the exact position of the extra carbon atom.

REPRINT NO. 4

INDIAN JOURNAL OF CHEMISTRY

Partial Synthesis of Dimethyl Dihydroceanothate from Methyl Betulonate

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The diosphenol (2b) obtained by the autoxidation of methyl dihydrobetulonate, on H_2O_2 oxidation followed by esterification affords the trimethyl ester (3b) of the seco-acid (3a). Dieckmann condensation of (3b) furnishes after purification methyl 2α-methoxycarbonyl-3-oxo-A(1)-norlupan-28-oate (1e) which on $NaBH_4$ reduction in methanol-dioxane gives the desired dimethyl dihydroceanothate (1d), identical with an authentic sample.

Ceanothic acid (1a)[1,2,3] was originally isolated by Julian et al from Ceanothus americanus and has since been isolated from a number of Australian Rhamnaceae species[5,6]. Huneck[7] in an attempt towards the partial synthesis of ceanothic acid developed a method for the synthesis of both epimeric A(1)-norlup-20(29)-en-3-carboxylic acids (1b) and (1c) by photochemical Wolff rearrangement of the diazoketone (2a). Kundu et al[8] also reported the synthesis of (1b).

We report here a successful synthesis of dimethyl dihydroceanothate (1b). Autoxidation of methyl dihydrobetulonate by passing a stream of oxygen in presence of K-tert. butoxide in tert. butanol gave the diosphenol (2b), m.p. 131-33°, $(\alpha)_D$ - 1.96°. The diosphenol on oxidation with 30% hydrogen peroxide gave the seco-acid (3a), m.p. 175-77°, ν_{max}^{nujol} 1690, 1710 (COOH) cm^{-1}. Treatment of (3a) with diazomethane

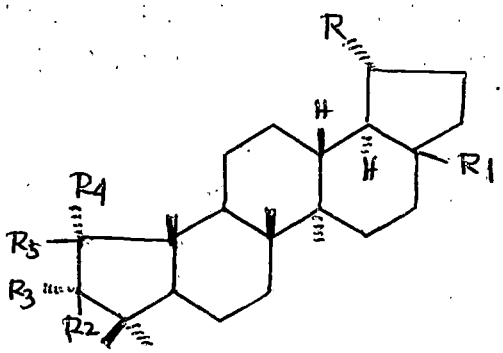
afforded the trimethyl ester (3b)[1,6], M.P. 146-47°, ν_{max}^{nuzol} 1745, 1725 cm^{-1} (CO_2Me). Dieckmann condensation of (3b) in the presence of potassium tert-butoxide in benzene under nitrogen blanket[9a,9b] gave a gummy product which on chromatography over alumina gave methyl 2α-methoxycarbonyl-3-oxo-A(1)-norlupan-28-oate(1e) m.p. 191-93°, $(\alpha)_D$ + 89°, ν_{max}^{nujol} 1750, 1720 cm^{-1}, and its epimer (1f) 175-77°, $(\alpha)_D$ + 42°, ν_{max}^{nujol} 1750, 1730 cm^{-1} in the ratio of 17 : 1. The high yield of the β-keto ester (1e) with the desired stereochemistry in this reaction is significant and is at variance with the observation of Dade et al.[3] who stated that methyl 2α-methoxycarbonyl-3-oxo-A(1)-norlup-20(29)-en-28-oate (dimethyl dehydrocanothate) was rapidly epimerized by alkali to an equilibrium mixture containing 40% of the starting material and 60% of the isomer epimeric at C-2.

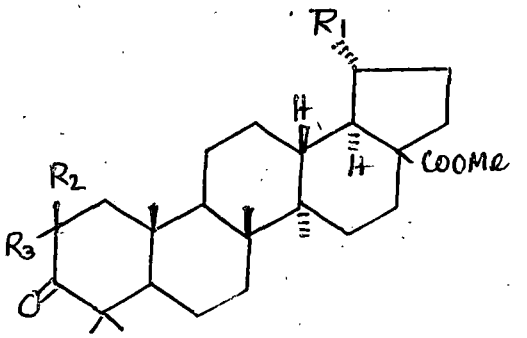
The β-keto ester (1e) on reduction with sodium borohydride in methanol-dioxane gave a mixture (two spots in TLC) which on chromatography over alumina first eluted (benzene-pet ether, 3:2) a solid, m.p. 261-63°, $(\alpha)_D$ + 22°, ν_{max}^{nujol} 3540, 1730, 1710 cm^{-1}, identical with an authentic specimen of dimethyl dihydroceanothate (1d) supplied by Prof. de Mayo. Further elution with the same solvent gave another solid, m.p. 140-42°, ν_{max}^{nunol} 3560, 1745, 1705 cm^{-1}. The yield of the material was not sufficient for NMR studies but by analogy with previous work[3] it is believed to the the C-3 epimer (1g). Further work is in progress to elucidate its stereochemistry.

Investigation was also initiated to prepare the β-keto ester (1e) by carbomethoxylation of the A-nor ketone (4b) at C-2. The diosphenol (2b) on treatment with 10% ethanolic sodium hydroxide solution underwent benzilic acid rearrangement to

furnish the α-hydroxy acid (4a), m.p. 255-56°, ν_{max}^{nujol} 3440, 3340, 1720 cm^{-1}. The latter on treatment with lead dioxide[10a,10b] in glacial acetic acid under mild reluxing conditions gave the nor-ketone (4b)[1,11], m.p. 179-80° $(\alpha)_D$ + 75.4°.

Attempts on carbomethoxylation of this ketone using dimethylacarbonate in the presence of sodium methoxide, potassium-tert butoxide or sodium hydride in various solvents proved unsuccessful.





1a, $R_1=R_4=COOH$, $R_2=OH$, $R=-C(CH_2)(CH_3)$, $R_3=R_5=H$

1b, $R_1=CH_3$, $R_3=COOH$, $R_2=R_4=R_5=H$, $R=-C(CH_2)(CH_3)$

1c, $R_1=CH_3$, $R_2=COOH$, $R_3=R_4=R_5=H$, $R=-C(CH_2)(CH_3)$

1d, $R_1=R_4=COOMe$, $R_2=OH$, $R_3=R_5=H$, $R=-C(CH_3)_2$

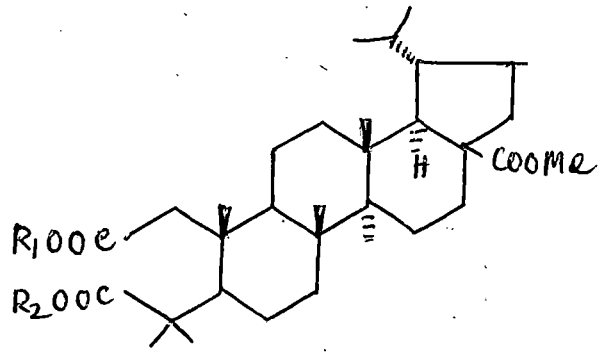
1e, $R_1=R_4=COOMe$, $R_2,R_3=O$, $R_5=H$, $R=-CH(CH_3)_2$

1f, $R_1=R_5=COOMe$, $R_2,R_3=O$, $R_4=H$, $R=-CH(CH_3)_2$

1g, $R_1=R_4=COOMe$, $R_3=OH$, $R_2=R_5=H$, $R=-CH(CH_3)_2$

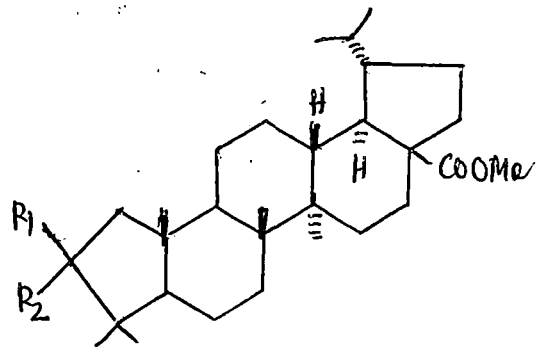
2a, $R_2,R_3=N_2$, $R=-C(CH_2)(CH_3)$

2b, $R_2,R_3=O$, $R_1=-CH(CH_3)_2$



3a, $R_1 = R_2 = H$

3b, $R_1 = R_2 = CH_3$



4a, $R_1 = OH$, $R_2 = COOH$

4b, $\begin{matrix} R_1 \\ R_2 \end{matrix} > = O$

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