on the basis of their spectral and physical properties and the identities confirmed by direct comparison with respective authentic samples.

Fraction II : On Crystallization from alcohol it afforded pure compound C as colourless needles, m.p. 206° and gave +ve LB test. The compound was identified as epi-lupeol since on Jones' oxidation it afforded lupenone and was itself different from lupeol.

Fraction III : It was chromatographed over Ag^+/SiO_2 to separate compounds D and E which crystallized from alcohol as needles, m.p. 199° and 212° respectively. They were identified as β-amyrin and lupeol respectively on the basis of their physical properties and spectral data.

Fraction IV : Column chromatography over Ag^+/SiO_2 separated compounds F and G, m.p. 138° and 169° respectively. They gave green colour in LB test and were identified as sitosterol and stigmasterol and the identity confirmed by direct comparison with respective authentic samples.

Chloroform extract : The extract was subjected to column chromatography over silica gel which yielded compounds H and I in addition to the small amounts of aforesaid compounds. The compounds crystallized from alcohol as needles, m.p. 238° and 258° respectively and gave +ve LB test. They were identified as erythrodiol and betulin on the basis of their spectral data and confirmed by direct comparison with respective authentic samples.

Alcohol extract : It contained leucoanthocyanins and the anthocyanidin produced by heating with alcohol hydrochloric acid was found to be cyanidin by direct comparison by paper chromatography. The leuco compound appeared to be highly polymeric and could not be studied further.

The occurrence of the compounds of lupene series and the corresponding compounds of biogenetically related oleanane series as pairs[1] separable by Ag^+/SiO_2 column chromatography only is interesting.

One of the authors (NK) wishes to thank CSIR of India, for fellowship.

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CHEMICAL CONSTITUENTS OF *UMBILICARIA INDICA* FREY AND *RAMALINA FARINACEA* L. ACH.

THE lichen *Umbilicaria indica*, Frey (Umbilicariaceae) was collected from the rocks near Govindaghat in the Chamoli District of the Western Himalayas. A survey of literature showed that the lichen was not previously studied for its chemical components. The dark brown coloured lichen (15 g) with dark pustules was dried, powdered and extracted with light petroleum ether (b.p. 60–80°), ether and acetone in succession. Traces of wax was found in the light petroleum ether extract. The ether and acetone extracts contained the same phenolic constituents (TLC) and therefore were mixed and evaporated to dryness. The residue was treated with water and the water insoluble part (0·18 g) was found to be a mixture of two phenolic components by TLC[1] (Silica gel-G ; benzene : dioxan : acetic acid, 90 : 25 : 4). Their R_f values corresponded to those of lecanoric and gyrophoric acids. They were separated by fractionation from acetone. The major component of the mixture was shown (UV, IR and TLC) to be lecarnoric acid, m.p. and mixed m.p. with an authentic sample of lecanoric acid, 174–6°. The minor component was shown (UV, IR and TLC) to be gyrophoric acid, m.p. and mixed m.p. with an authentic sample, 220° d. The water soluble portion of the acetone extract was treated with Norit and the aqueous solution filtered. On concentration it gave a small amount of residue having mannitol (paper chromatography)[2].

Ramalina farinacea L. Ach. (Usneaceae) was collected from trees near Eturu Nagaram in Warangal District, India. Survey of literature[3] showed that various samples of this lichen yielded divergent results. In the present case 50 g of the powdered lichen was extracted as in the previous case. The light petroleum extract yielded (+)-Usnic acid, m.p. 203–4° ; $[\alpha]_D$ + 493° (*c*, 1·0 in chloroform) (0·15 g, 0·3%) identified by a direct comparison with an authentic sample. The ether extract yielded a colourless compound (0·1 g., 0·2%) which crystallised from 80% acetone as needles, m.p. 172–3°. Its homogeneity was revealed by TLC. The acetone extract was evaporated to dryness and the residue (1·5 g) extracted with hot water. The water insoluble residue revealed the presence of two phenolic compounds by TLC, the one with the higher R_f value being identical with the compound obtained from the ether extract. The solid was repeatedly washed with ice-cold acetone. The acetone solution on evaporation gave a residue (1·2 g, 2·4%) which on repeated recrystallisation from 80% acetone gave colourless needles, m.p. 172–3°. The com-

pound was identical with the ether compound (Found : C, 61·2 ; H, 5·2 : Calc. for $C_{17}H_{16}O_7$: C, 61·4 : H, 4·8%). Its colour reactions and spectral data[1-5] (UV, IR and NMR) indicated the compound to be evernic acid. It was subjected to menthanolysis with 5% methanolic KOH at 40° C in nitrogen atmosphere for 2 hours and the acid and the ester components isolated as usual. The methanolysis products were identified (m.p., mixed m.p., TLC, UV, IR and elemental analysis) as methyl everninate and orsellenic acid. This confirmed the identity of the compound as evernic acid.

The acetone insoluble residue (0·1 g, 0·2%) was recrystallised from 80% acetone to obtain wooly needles, m.p. 198° (Found : C, 62·1 ; H.5·6 : Calc. for $C_{18}H_{18}O_7$: C, 62·4 ; H, 5·2%). Light absorption in ethanol : max. at 275 and 306 nm (log ϵ : 4·33 and 4·03. Main IR bands : ν_{max}^{nujol} 3509 (phenolic OH), 1667 (chelated depside carbonyl), 1639 (chelated carboxy carbonyl) cm^{-1}. It gave a violet ferric reaction and a positive homofluorescein reaction. It formed an yellow solution with conc. HNO_3 and a pale pink solution on standing with alkali. These properties indicated that the compound might be obtusatic acid. The methyl ester of the acid (brief treatment with diazomethane in ether solution) crystallised from methanol as colourless needles, m.p. 175° (Lit. m.p. for methyl obtusate[6], 175°) and acetylation of the acid (acetic anhydride–H_2SO_4) gave the acetyl derivative which separated from ethyl acetate–light petroleum ether as prisms, m.p. 172–4[6] (Lit.[6] m.p. 175°). Its methyl ester dimethyl ether (diazomethane–methanol/ether ; 48 hr) crystallised from methanol as colourless needles, m.p. 126–127° (Lit.[6] m.p. 127°) (Found : C, 64·7 ; H, 6·4 : Calc. for $C_{21}H_{24}O_7$: C, 64·9 ; H, 6·2%). The NMR spectral data of the methyl ester dimethyl ether clearly indicated the various protons of the different functional groups. Comparison with an authentic sample of obtusatic acid[7] confirmed their identity. Incidentally this is the first report of the occurrence of obtusatic acid in the Indian lichens.

The water soluble portion of the acetone extract was treated with Norit, filtered and the filtrate evaporated. The residue (0·05 g., 0·1%) was triturated with cold absolute methanol and filtered. The residue crystallised from methanol–absolute ether as colourless crystals, m.p. 102°. It was identified as D-arabitol by paper chromatography[2] and by a direct comparison with an authentic sample.

The authors are grateful to Dr. D. D. Awasthi, for the identification of the lichens, Prof. N. V. Subba Rao, Hyderabad, for the microanalysis and the spectral data, Dr. S. Huneck, for an authentic sample of obtusatic acid, Prof. E. V. Sundaram and the Principal, R.G. Centre, Warangal, for the facilities. Financial assistance from the U.G.C., New Delhi, is gratefully acknowledged.

Department of Chemistry, Post-Graduate Centre (O.U.), Warangal 506 009 (A.P.), *October* 18, 1975.

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CHEMICAL EXAMINATION OF LEAVES OF *BARRINGTONIA ACUTANGULA* GAERTN.

Several polyhydroxy triterpenes were isolated in the past from the various parts of *Barringtonia acutangula* Gaertn[1-4]. We now describe the isolation and structural elucidation of a new trihydroxy triterpene monocarboxylic acid, now named acutangulic acid, from its leaves, in which it is accompanied by stigmasterol-β-D-glucoside and barringtogenic acid (I).

Acutangulic acid (II) $C_{30}H_{48}O_5$, m.p. 290–1°, $[\alpha]_D$ + 15°, diacetate (III) m.p. 188–9° $[\alpha]_D$ – 35°, methylester diacetate (IV) m.p. 219–20°, has a *trans* glycolic function (1 mole of periodate in 4–6 hrs.) which can be located at 2 α, 3 β from its NMR spectrum. The hydrogen on the 2 α-acetoxyl appeared as an ill-defined quartet at δ 5·05, 5·12, 5·20, 5·28 *J* 4, 9 Hz and the proton on 3 β-acetoxyl as a doublet at δ 4·8, 4·9 *J* 9 Hz. This is in close agreement with a number of 2 α, 3 β-dihydroxy triterpenes occurring in nature[5].

The third hydroxyl could not be acetylated even under forced conditions (with perchloric acid) and diacetyl methyl acutangulate exhibited a singlet resonance at δ 2·6 in its NMR spectrum indicating its tertiary character. It is further supported by its unusual resistance towards pyridine-CrO_3 or CrO_3–AcOH. But with the latter reagent after prolonged reaction, an α : β-unsaturated ketone (V) was obtained, m.p. 165° IR 3540 (–OH) and 1650 cm^{-1}. Obviously, the ketone could be 11-keto $\Delta^{12:13}$ methyl diacetylacutangulate.