the mixtures were taken in a Philips Debye-Scherrer camera of 57·3 mm diameter. Rich Seifert X-ray unit, with nickel-filtered copper radiation was employed for this purpose. The intensities of the 110, 112 and 114 reflections of vaterite, corresponding to the spacings 3·540 Å, 3·270 Å and 2·715 Å and the 104 reflection of calcite corresponding to the *d*-spacing, 3·035 Å were determined by microdensitometry. Figure 1 shows

FIG. 1. Microdensitometer plots of the 110, 112, 114 reflections of vaterite and 104 reflection of calcite in standard mixtures.

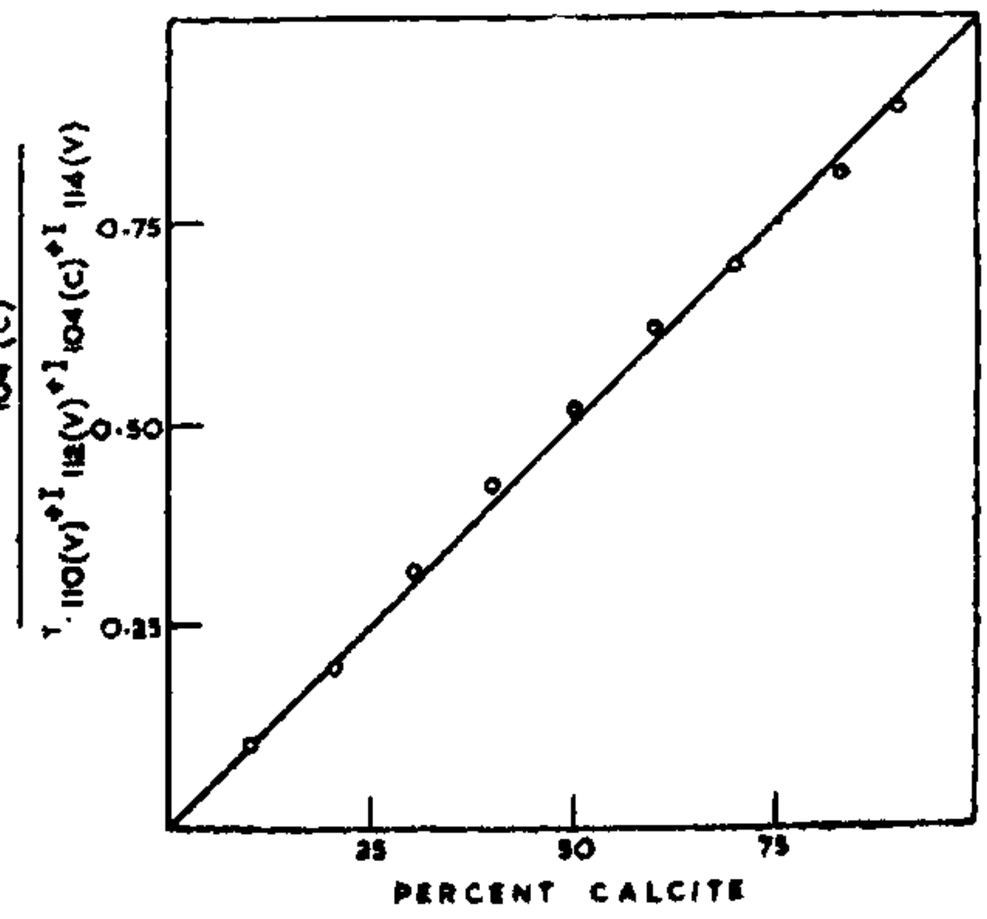

FIG. 2. Calibration graph for the analysis of mixtures of vaterite and calcite.

the densitometer traces of some of the mixtures measured using photovolt transmission density unit and the multiplier photometer model 520-M. In this model full-scale deflection in the most sensitive range corresponds to 0·01 microlumen. The relation between the intensity ratios of the different reflections of vaterite and calcite and the fraction of calcite in the mixture is represented in Fig. 2. From this it is evident that the relation between intensity of reflections and the fraction of calcite in the mixture is given by

$$f_c = \frac{I_{104\,(c)}}{I_{110\,(v)} + I_{112\,(v)} + I_{104\,(c)} + I_{114(v)}}$$

where c and v stand for calcite and vaterite respectively.

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CHEMICAL INVESTIGATION OF INDIAN LICHENS

Part XXXI. Terpene Acids B and D from *Lobaria* Species

THE isolation of four crystalline terpenic compounds A, B, C and D from the different species of *Lobaria* lichens collected from the Western Himalayas were earlier reported[1a]. Of them, A. B and D were major components. The structure of compound A called retigeradiol was later proposed[2] as 3 β, 19 β-dihydroxytaraxerane.

Compound B (Retigeranic Acid)[1b]

This has been obtained from *L. retigera* and *L. subretigera* samples in yields varying from 0·03 to 2·84%. It crystallised from acetone-dioxane as long, colourless lances, m.p. 218–21° $[\alpha]_D$ — 59° (*c*, 1·0 in $CHCl_3$). Elemental analysis and mass spectrum (M^+, 370) established its molecular formula as $C_{25}H_{38}O_2$. In Lielermann-Buchard test it gave a red solution with green fluorescence; Salkowski's test produced yellow colour changing to orange-red. $\nu_{max.}^{KBr}$ 2985(s), 2915(s), 2632(m), 1675(s), 1618(s), 1538(m), 1508(m), 1460(s), 1418(s), 1379(s), 1300(s), 1276(s), 1258(s) and 1053 (broad, s) cm^{-1}.

The carbonyl frequency at 1667 cm^{-1} showed the presence of an α, β-unsaturated carboxyl group and this was supported by u.v. absorption at 239 nm (log ϵ 3·92). The acid gave an yellow colour

with TNM and decolourised bromine in carbon tetrachloride.

Methylation with diazomethane gave the ester as a glassy solid which could not be crystallised; $\lambda_{max.}$ 241 nm (log ϵ 3·37). $LiAlH_4$ reduction of retigeranic acid and of its ester yielded an alcohol which crystallised as colourless prisms from ethanol, m.p. 105–07° $[\alpha]_D$ −22° (*c*, 1·0 in $CHCl_3$). It analysed for $C_{25}H_{40}O$ (M^+, 356). It answered TNM test for unsaturation. $\nu_{max.}^{nujol}$ 3731(s), 3597(s), 1603(w), 1587(w), 1548(w), 1527(w), 1515(w), 1323(m), 1285(s), 1266(m), 1247(s), 1202(m), 1174(m), 1149(m), 1068(w), 1029(s), 1012(s), 1002(s), 985(s), 962(m), 952(w), 935(w), 893(w), 877(w), 840(w), 812(w) and 790 cm^{-1}.

The n.m.r. spectra of the carboxylic acid and its derivatives revealed the presence of five tertiary methyls between δ 0·9 and δ 1·0. The position of the signals for $-CO_2CH_3$, $-CH_2OH$ and $-CH_2OAC$ at δ 3·73 (s, 3 H) δ 4·16 (broad singlet, 2 H) and δ 4·67 (*d*, J = 4 Hz, 2 H), supported the presence of an α,β-unsaturated carboxyl group. Further, the spectra did not show any signal due to vinyl hydrogen β- to the carboxyl group or any other olefinic protons. These features and especially the presence of the five tertiary methyls coupled with its molecular formula suggested the probability of the compound being a new sesterterpenic acid.

Compound D

This was obtained from the ether extracts of various *Lobaria* lichens, the yields varying from 0·03 to 1·36%[3]. It crystallised from glacial acetic acid as colourless needles, m.p. 289–91°, $[\alpha]_D$ + 21° (*c*, 1·15 in pyridine). Elemental analysis agreed with the molecular formula $C_{30}H_{48}O_4$. It was insoluble in most of the organic solvent but readily dissolved in pyridine and dimethyl formamide. It gave a pink colour in Liebermann-Burchard test and an yellow colour changing to pale orange in the Salkowski test. If answered TNM test for unsaturation. $\nu_{max.}^{KBr}$ 3472(s), 2960(s), 1706(s), 1639(s), 1626(s), 1563(w), 1466(m), 1449(m), 1439(m), 1408(m), 1170(s), 1133(s), 1083(s), 1050(s), 971(s), 905(m), and 860(w) cm^{-1}.

When methylated with CH_2N_2, compound D yielded a methyl ester which crystallised from ethyl acetate as small colourless needles, m.p. 244–60°; $[\alpha]_D^{24°}$ −2·8° (*c*, 1·3 m in $CHCl_3$). Its elemental analysis and methoxyl estimation agreed with the molecular formula $C_{31}H_{50}O_4$ with one methoxyl group. $\nu_{max.}^{KBr}$ 3472(s), 2985(s), 1724(s), 1626(m), 1587(m), 1481(m), 1449(s), 1412(w), 1379(m), 1250–1235 (broad, s), 1205(s), 1053(s), 1014(s), and 971(s) cm^{-1}.

By the action of acetic anhydride and pyridine at 40° for 24 hours the acid gave a diacetate as a colourless solid, m.p. 286–88°, $[\alpha]_D^{26°}$ − 18° (*c*, 1·18 in $CHCl_3$).

By similar treatment of the methyl ester, the methyl ester diacetate was obtained as a colourless solid, m.p. 130–32°, $[\alpha]_D$ 25·5° $\nu_{max.}^{CHCl_3}$ 2985(s), 2915(sh), 1745(s), 1661(w), 1572(w), 1473(m), 1458(m), 1439(m), 1379(s) 1370(s), 1302(m), 1242(s), 1176(m), 1163(m), 1143(m), 1064(m), 1047(m), 1026(m), 997(m), 970(m), 943(w), 912(w), 901(m), 891(w), 866(w), 836(w) and 826(w) cm^{-1}.

By the reduction of the ester with $LiAlH_4$ in dry THF (reflux) the corresponding alcohol was obtained and it crystallised from acetone as colourless, long feathery needles, m.p. 250–56°: $[\alpha]_D^{22°}$ − 33·5° (*c*, 1·8 in $CHCl_3$).

Recently Prof. Shibata has communicated to us that compound D has been studied by him also and the structure of 2-α, 3-β-dihydroxy fern 9, 11-ene-23-oic acid proposed for it and it has been named retigeric acid. The properties recorded by us agree with this structure. Further, the structure of retigeranic acid has been arrived at by him as a novel sesterterpene by X-ray analysis.

Our thanks are due to Dr. R. Seshadri for help in preparing the manuscript.

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A NEW CHROMENOCHALCONE BAVACHROMENE FROM THE SEEDS OF *PSORALEA CORYLIFOLIA*

From time to time the fruits of *Psoralea corylifolia* have been examined and a large number of compounds have been reported[1]. We were interested in this drug to know the contribution of the two important portions, (1) the soft sweet smelling and coloured outer mesocarp and (2) the hard nut with its kernel containing fats and other components. Our earliest work showed that the latter portion contains all the psoralen and isopsoralen and the other components should therefore be considered to be in pericarp. But there was no