

scalar boson octet by itself, or of predicting the octet and the decuplet in meson baryon scattering, etc. Through this kind of work, initiated by Capps, Cutkosky, and Martin and Wali, one hopes to understand how symmetries arise, and how they are broken. The tools one uses in these investigations are the analyticity properties of the S-matrix, and general properties like unitarity and crossing symmetry. However, at present, one is forced to introduce very drastic

simplifying approximations in carrying out the programme, even in single channel problems, and all the more so in the multi-channel problem relevant to the question of symmetries. The semi-quantitative success achieved so far has therefore been very encouraging, and has stimulated considerable activity in this field. If these attempts succeed, one will have travelled quite far from one's naive conception of what elementary particles are.

## CHEMICAL COMPONENTS OF THE LOBARIA LICHENS FROM THE WESTERN HIMALAYAS

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**A**MONG lichens, members of the genus *Lobaria* are generally found in abundance on the Himalayas at altitudes above 8,000 ft. They are foliose, fairly large in size and are readily recognised by the presence of white spots on a dark violet background when dry and olive-green when moist. They have been considered to be important in perfumery and tanning and have been used as vegetable drugs for the cure of eczema and for lung troubles.

In an earlier investigation<sup>1</sup> of the lichen *Lobaria isidiosa* from Darjeeling, it was found to contain a triterpene and thelephoric acid, a

these cases have been compared with the above four terpenoids.

### *Lobaria isidiosa*

Of the two samples of *L. isidiosa* now examined, one was collected near Darjeeling (8,000 ft.) during the summer of 1961 while the other was collected in June 1962 from a pine tree near Ganghariya (10,000 ft.) in Western Himalayas. The general extraction procedure adopted was the same as described by Aghoramurthy *et al.*<sup>4</sup> The results are presented in Table I, and the details of separation and identification are given below.

TABLE I  
Chemical components of *L. isidiosa*

Year and place of collection	Petroleum extract (Yield %)	Ether extract	Acetone extract
1961 Darjeeling ..	Wax and carotenoids	(i) Triterpene (D) (0.57%) (ii) Stictic acid (0.38%)	(i) Thelephoric acid (0.23%) (ii) Stictic acid (0.51%) (iii) D-Mannitol (0.20%)
1962 Ganghariya ..	"	(i) Triterpene (D) (0.40%) (ii) Stictic acid (0.28%)	(i) Thelephoric acid (0.17%) (ii) Stictic acid (0.24%) (iii) D-Arabitol (0.17%)

dark violet quinone pigment. Aghoramurthy, Sarma and Seshadri<sup>2</sup> used this lichen as a source of thelephoric acid for a detailed study of its constitution. Samples collected during the summers of 1953, 1958 and 1959 showed variation in their chemical components.<sup>3</sup> The presence of fairly good amounts of terpenoid compounds was noted in this lichen and four terpenoids A, B, C and D were recorded. This prompted us to study other samples of this and other *Lobaria* species collected mainly from the Western Himalayas. The terpenes isolated in

Petroleum ether extract was concentrated and chromatographed on alumina. Elution with various solvents gave only wax and carotenoids with both lichen samples.

Ether extract was evaporated to dryness. Preliminary examination showed that it consisted of a phenolic and a non-phenolic compound separable with 80% acetone. Hence the mixture was repeatedly extracted with boiling 80% acetone. The extract on concentration yielded a colourless solid which on repeated crystallisation from 80% acetone gave stictic

acid, m.p. and mixed m.p. 267-69° d.; tetraacetate, m.p. 226-27°. The acetone insoluble residue was colourless and non-phenolic. It was sparingly soluble in alcohol, ether, benzene and chloroform and readily in pyridine. It crystallised from boiling glacial acetic acid as colourless needles, m.p. 289-91°,  $[\alpha]_D^{25} + 21'$  (C, 1.0 in pyridine). It gave a pink colour in the Liebermann-Burchard test and analysed for  $C_{31}H_{50}O_5$ . That it is a terpenoid hydroxy acid was shown by the preparation of its acetate, m.p. 286-88°, and its methyl ester, m.p. 244-46° which gave yellow colour with tetranitromethane in chloroform indicating unsaturation. Agarwal *et al.*<sup>3</sup> reported the presence of a triterpene (compound-D) m.p. 267-69° from *L. isidiosa* collected from Darjeeling in 1959; crystallisation of this compound twice from glacial acetic acid raised the m.p. to 289-91°; methyl ester, m.p. 244-46°. A direct comparison of the two samples and their methyl esters confirmed their identity.

Acetone extract was concentrated and the dark violet solid was filtered off. It was extracted exhaustively with 80% acetone and

pentoxide crystallised from dry methanol-ether mixture. The first lichen sample gave D-mannitol, m.p. 162-64° (hexaacetate, m.p. 122-24°) while the second yielded D-arabitol, m.p. 101-02° (pentaacetate, m.p. 76°). The mother liquors in each case did not show the presence of any second alcohol.

#### *Lobaria retigera*

Morphologically both *L. isidiosa* and *L. retigera* look alike except that the latter is much darker on its reverse side than the former. A Japanese sample of *L. retigera* was earlier examined by Asahina *et al.*,<sup>5</sup> who obtained thelephoric acid (0.013%) along with a colourless unknown acid. Indian samples have not been examined earlier. Four collections were made from the following places during the summer of 1962: (1) Valley of flowers (12,500 ft.), under the 'Rutba' plants. (2) Ganghariya (10,000 ft.), from rocks. (3) Ganghariya, from the pine trees and (4) On the way to Hemkund-Lokpal (13,500 ft.) under the 'Rutba' plants. The method of extraction was the same as for *L. isidiosa* and the compounds and their yields are recorded in Table II.

TABLE II  
Chemical components of *L. retigera* collected during June, 1962

Place of collection	Petroleum ether extract	Ether extract	Acetone extract
Valley of flowers ..	Wax, carotenes and triterpene-(A) (0.011%)	(i) Triterpene (D) (0.46%) (ii) Thelephoric acid (0.065%)	(i) Thelephoric acid (0.22%) (ii) Stictic acid (0.34%) (iii) D-Mannitol (0.46%) (iv) Arabitol*
Ganghariya (from Rocks)	(i) Triterpene-(A) (0.27%) (ii) Terpenoid acid-(B) (2.4%)	Triterpene-(D) (0.03%)	(i) Thelephoric acid (0.19%) (ii) Stictic acid (0.11%) (iii) D-Arabitol (0.17%) (iv) Mannitol*
Ganghariya (from pine trees)	(i) Triterpene-(A) <sup>a</sup> (0.059%) (ii) Terpenoid acid (B)-(0.47%)	Stictic acid (1.0%)	(i) Thelephoric acid (0.18%) (ii) Stictic acid (0.53%) (iii) D-Arabitol (0.53%) (iv) Mannitol*
Hemkund Lokpal	(i) Triterpene-(A) (0.29%) (ii) Terpenoid acid-(B) (2.75%)	Triterpene-(D) (0.057%)	(i) Thelephoric acid (0.29%) (ii) Stictic acid (0.043%) (iii) Arabitol*

\* Compounds identified paper chromatographically.

the residue crystallised from hot pyridine to yield brilliant dark violet crystals, not melting below 360°, identified as thelephoric acid by direct comparison with authentic sample.

The combined filtrate was evaporated to dryness and the residue extracted with hot water. The insoluble part on crystallisation from 80% acetone gave stictic acid, m.p. and mixed m.p. 267-69° d. The water extract was concentrated on a water-bath to get a syrupy liquid which after drying over phosphorous

Light petroleum extract of sample 1 was concentrated and chromatographed on alumina. Elution with different solvents gave wax, carotenoids and a colourless substance (A). The extracts of samples 2, 3 and 4 were concentrated and left overnight whereby (A) separated as a colourless solid. The mother liquor on further concentration gave another colourless crystalline solid (B).

(A) crystallised from chloroform as colourless prisms, m.p. 270-73°,  $[\alpha]_D^{25} + 28'$  (C, 0.5 in

chloroform). Colour reactions indicated it to be a saturated triterpene,  $C_{30}H_{52}O_2$ . That it is a diol was shown by the preparation of its diacetate, m.p. 276–79° and dibenzoate, m.p. 304–06°. It was identified as triterpene (Compound-A) earlier obtained by Agarwal *et al.*<sup>3</sup> from *L. isidiosa* by direct comparison.

(B) crystallised from dioxan-acetone as colourless long needles, m.p. 218–21°,  $[\alpha]_D - 59^\circ$  (C, 1.0 in chloroform). It was non-phenolic and gave an orange red colour with a green fluorescence in the Liebermann-Burchard test. That it is an  $\alpha\beta$ -unsaturated carboxylic acid was shown by its I.R. spectrum ( $\nu_{\max}$ , 1667  $cm^{-1}$ ) and U.V. absorption ( $\lambda_{\max}$ , 239  $m\mu$ ;  $\log \epsilon$  3.92). It was identical with the "Compound-B" described by Agarwal *et al.*<sup>3</sup>

Ether extract of sample 1 on evaporation gave a light violet mixture of thelephoric acid and a triterpene acid. Separation was effected taking advantage of the fact that thelephoric acid forms a blue-coloured water soluble complex with borax. The mixture was macerated with a concentrated solution of borax, the suspension filtered and the colourless residue washed with borax solution and water. The residue gave colour reactions of triterpenes and crystallised from glacial acetic acid as colourless needles, m.p. 289–91°. Its identity with the triterpene (D) obtained earlier from *L. isidiosa* was shown by mixed fusion and the identity of I.R. spectra; their methyl esters were also found to be identical. The borax solution of the thelephoric acid on acidification deposited the acid as a

blue powder. Samples 2 and 4 also gave only compound-D from their ether extracts and no thelephoric acid whereas sample 3 did not give (D) and gave only stictic acid.

Acetone extract was studied in the same way as in the case of *L. isidiosa* and it gave thelephoric acid, stictic acid, D-arabitol and D-mannitol in all the four samples. Of the two sugar alcohols, only one could be isolated in each case while the presence of the other was detected by paper chromatography.

As will be clear from Tables I and II, there is general resemblance in the phenolic components of the various *Lobaria* samples examined but there are variations in the terpenoid components. Compound (A) is a diol, compound (B) an  $\alpha\beta$ -unsaturated terpenoid acid and compound (D) is an unsaturated triterpene acid. It may be mentioned that the triterpene acid (Compound-C), m.p. 318–20°, reported by Agarwal *et al.*<sup>3</sup> from *L. isidiosa* has not been detected in the course of the present work. A detailed study of the compounds (A), (B) and (D) is in progress.

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2. Aghoramurty, K. A., Sarma, K. G. and Seshadri, T. R., *Tetrahedron Letters*, 1959, 8, 20; *Ibid.*, 1960, 16, 4.
3. Agarwal, S. C., Aghoramurty, K. A., Sarma, K. G. and Seshadri, T. R., *J. Sci. Industr. Res.* 1961, 20 B, 613.
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5. Asahina, Y. and Shibata, S., *Ber.*, 1939, 72, 1531.

## RAMAN SPECTRUM OF GALLIUM PHOSPHIDE

RECENTLY considerable interest has been shown in the interpretation of the infra-red lattice absorption of crystals in terms of two-phonon interactions. A method of obtaining complementary information on the subject is to study the Raman scattering in typical crystals involving two-phonon processes. Results of such a study on the Raman spectra of gallium phosphide, using the 6328 Å output of a helium-neon laser have been reported. This is the first time that a Raman spectrum has been measured for a III-V semiconductor. So far no Raman measurements have been made on III-V semiconductors because of the lack of suitable sources with photon energies less than the band gap of the semiconductor.

The sample was a zone-refined polycrystal of good optical quality. The laser beam of the He-Ne laser with a uniphase output of 30 mW

c.w. was passed vertically through the gallium phosphide crystal, and the light scattered at right angles was examined with a f/6 Hilger and Watts Raman spectrograph.

In the Raman scattering process the first-order spectrum, which involves the creation or destruction of single phonons, is not so strong, does not obscure the two-phonon spectrum, and establishes the energies of the longitudinal (LO) and transverse (TO) optic branches at the centre of the zone. An analysis of the second-order Raman spectrum shows a number of lines which have been assigned to two-phonon interactions. Two prominent peaks at 782  $cm^{-1}$  and 736  $cm^{-1}$  correspond to the optical phonon energies of 391  $cm^{-1}$  (TO) and 368  $cm^{-1}$  (LO) at the zone centre.—[*Physics Letters* (Amsterdam), 1 November 1964.]