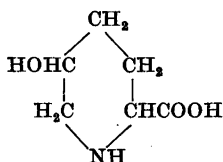


and phenol-NH₂). Because we do not know to what extent the position of the OH group in the ring influences the R_F -value we do not consider the identical chromatogram given by compound C and 5-hydroxy-piperidine-2-carboxylic acid a conclusive proof for the identity of these substances. Oxidation with permanganate in 20 % sulphuric acid solution at 10° C gave mainly glutamic acid and aspartic acid in smaller amounts. On the basis of this we may conclude that in the hydroxy-piperidine-carboxylic acid which we have isolated the OH group actually is in the position 5 and the carboxyl group in the position 2. The formation of glutamic acid cannot be explained otherwise.



It is possible that the new amino acid is formed from δ -hydroxylysine.

We are very grateful to Professor T. J. King, Nottingham, for a preparation containing some 5-hydroxy-pipecolic acid, to Dr. G. Curzon, Stanmore, England, for the isonipecotic acid (piperidine-4-carboxylic acid), to Mr. O. Oja for helping us in the preparation of nipe-cotic acid (piperidine-3-carboxylic acid), and to Professor A. Kalela for the plant material we got from the University Botanical Garden.

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Triterpenoids in Lichens II. Taraxerene, a Naturally Occurring Triterpene

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During our researches on lichens a sample of *Cladonia deformis* Hoffm. was investigated. The origin of the sample has been reported previously¹. The general procedure for extraction with ether and working up of the extract has been reported in part I of this series².

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The neutral part of the ether extract, when chromatographed on alumina furnished a petroleum (b. r. 40–70°) eluate, which contained a hydrocarbon mixture (0.3 g) that did only partly melt on the boiling water-bath. The high-melting part of the fraction was much less soluble in petroleum than the low-melting one, and by taking advantage of this fact a sample of m. p. 230–233°, $[\alpha]_D + 4^\circ$ (c, 0.83) was obtained*. A much better separation, however, was achieved by careful chromatography: The hydrocarbon, dissolved in petroleum, was brought on a column of 30 g of alumina, 17 cm high, 1.5 cm diameter, and fractions of 5 ml were collected. The high-melting hydrocarbon was retained more tenaciously than the low-melting one, and thus a satisfactory separation could be obtained. For further purification the hydrocarbon was treated with petroleum, and finally the substance was crystallised from ether, m. p. 237–238°, $[\alpha]_D + 1^\circ$ (c, 0.81). The total amount of hydrocarbon was about 15 mg from 2.9 kg of dry lichen.

The manner in which the substance was obtained seemed to justify the assumption that it was a hydrocarbon, and the high m. p. suggested a polycyclic one. A triterpene** was not ruled out, and inspection of the literature indicated that identity with skimmene IIa³ might exist. The chemistry of taraxerol (skimmol) is presently being investigated by Dr. C. J. W. Brooks, compare⁴. Dr. Brooks incidentally learned of this possible identity through Dr. P. de Mayo, and very kindly provided a sample of taraxerene, which, although, strictly speaking, it has not been proved, is very likely identical with skimmene IIa,^{***} and which he had recently prepared by Wolff-Kishner reduction of taraxerone, and for which he reported m. p. 238–240° (strong sublimation), $[\alpha]_D + 3^\circ$, very sparingly soluble in chloroform, in agreement with our observations on the hydrocarbon from *Cl. deformis*. Taken at the same time the hydrocarbon from the lichen,

* All rotations in chloroform in a 1 dm tube.

** For nomenclature compare Barton, D.H.R. in Simonsen, John, *The Terpenes*, Vol. III, Cambridge 1952, p. 328.

*** Note added in proof: Weissenberg diagram of skimmene II a, very kindly provided by Dr. K. Takeda, showed identity with taraxerene.



Fig. 1. A. Hydrocarbon from *Cladonia deformis*. B. Taraxerene.

taraxerene and a mixture of the two all melted at 238–239°, thereby confirming the identity. A further confirmation of identity was obtained by X-ray powder diagrams of the two substances (Fig. 1) and Weissenberg diagrams. The measurements were very kindly carried out by Mr. O. Borgen (Theoretical Chemistry Department).

It is a curious fact of experience that when proceeding from monoterpenoids through triterpenoids hydrocarbons become progressively more rare, and as far as this author is aware no cyclic triterpene has hitherto been reported to occur in nature*. The only indication that such a one might be found in lichens are reports by Hesse⁵ and Zopf⁶ that *Nephroma arcticum* (L.) Forss., *N. lusitanicum* Schaer. and *N. laevigatum* Ach. contain nephrine, m. p. 168°, which Hesse⁵ considered to be a diterpene crystallising with one molecule of water. If this may be construed as evidence for the presence of a terpene in lichens, the reported m. p. would probably indicate a triterpene rather than a diterpene. When considering this problem, it should be taken into account that it may be questionable whether the analytical technique at that time permitted any greater accuracy on the scale that Hesse had to work (ca. 40 mg) when analysing his nephrine. In the writer's opinion it seems more probable that an oxygenated compound may have been present.

So far 5 triterpenoids are known to occur in lichens: ursolic acid⁷, zeorin⁸, leucotylin⁹, friedelin and epifriedelinol² and now taraxerene. Of these only ursolic acid and taraxerene have fairly well established constitutions, the former being related to α -amyrin¹⁰, the latter a stereoisomer of germanicene, with the C/D ring junction *cis* instead of *trans*², i. e. it belongs in the β -amyrin series.

* The triterpene squalene is of the alifatic type.

The author is glad to have this opportunity to express his gratitude to Professor N. A. Sørensen for help in collecting the lichen and for the interest he has taken in the work.

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The Biosynthesis of Riboflavin in *Eremothecium ashbyii*

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The hypothesis of MacLaren¹ that a substance with purine structure is utilized for the synthesis of riboflavin by *E. ashbyii*, is supported by recent work by Goodwin and Pendlington² and by Klungsöyr³.

Previous studies have shown that the carboxyl group of acetic acid is incorporated into the position 2 of the isoalloxazine part of the riboflavin molecule². This observation was taken as indirect evidence of the utilization of a purine intermediate