tes Pigment ophiolithischer Herkunft zurückzuführen. Als Materialspender fallen Serpentine und Peridotite in Betracht, deren Förderung syn- oder prae-oberjurassisch erfolgte (GRUNAU[6], GEES[4]).

b) Die oberjurassischen Südtessiner Radiolarite zeichnen sich aus durch das Fehlen typisch lauchgrüner Farbtöne, durch einen Cr-freien und Ti-armen Spurenelementbezirk und einen beträchtlichen Karbonatanteil. Ein direkter oder indirekter Ophiolitheinfluss hat sich hier nicht bemerkbar gemacht.

c) Die Grünfärbung einiger oberjurassischer Radiolarite der Simmen-Decke ist durch ein Farbpigment unbekannter Herkunft bedingt. Es wäre vielleicht zu denken an ein prae-triasisches, kristallines Liefergebiet oder an einen jurassischen Ophiolith-Anteil der Simmen-Decke, der allerdings heute vollständig wegerodiert ist. Die spärlichen Reste von Albit-Diabasen sind bekanntlich jünger als Cenoman und älter als Priabon (ARBENZ[7], GRUNAU[8]) und stehen somit in keiner Beziehung zur Grünfärbung.

H. R. GRUNAU und TH. HÜGI

Geologisches Institut und Mineralogisch-Petrographisches Institut der Universität Bern, den 2. Mai 1957.

Summary

The trace element content of a few Swiss ophiolites, radiolarian cherts and marls has been determined by means of spectrographic methods.

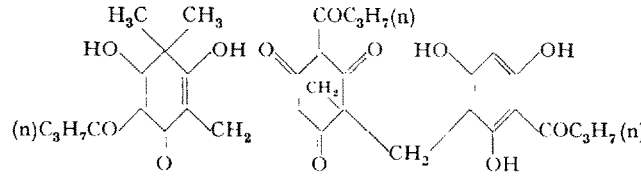
Field observations, microscopical and spectrographical data lead to the conclusion that the colour of green cherts in certain areas is due to the supply of clastic peridotite- and serpentine-particles originating from a syn-temporaneous ultrabasic igneous body.

[6] H. GRUNAU, Eclogae geol. Helv. *39*, 258 (1947).
[7] K. ARBENZ, Beitr. geol. Karte Schweiz [N.F.] *89*, 41 (1947).
[8] H. GRUNAU, Schweiz. min. petrogr. Mitt. *25*, 325 (1945).

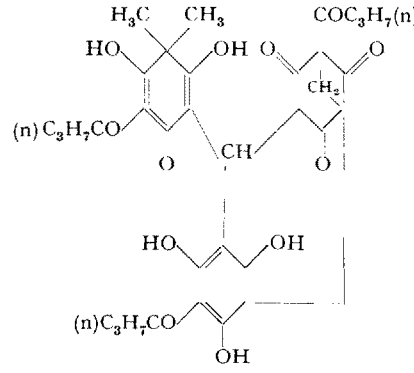
The Constitution of Filixic Acid

BOEHM[1] has proposed the alternative structures I and II for filixic acid, a major, biologically-active constituent of the resin of *Aspidium Filix mas*. These structures were based largely on the fact that filixic acid is hydrolysed by zinc dust and alkali to a mixture of butyric acid, filicinic acid (III, R = H) 1:3:5-trimethylphloroglucinol and *n*-butanoylfilicinic acid (III, $R = -COCH_2CH_2CH_3$). The yields of the filicinic acids produced on hydrolysis indicated that at least two filicinic acid moieties were present in the filixic acid molecule.

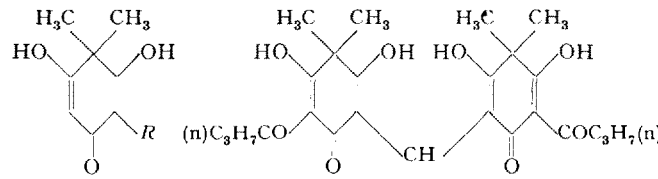
Also, albaspidin (IV) was obtained when filixic acid was refluxed for a prolonged time with ethanol. *Bis*-benzeneazophlorobutyrophenone was formed when filixic acid was treated with diazoaminobenzene. These degradation experiments suggested that filixic acid contained two *n*-butanoylfilicinic acid units, as in albaspidin, combined with a single phlorobutyrophenone unit. In order to account for the formation of 1:3:5-trimethylphloroglucinol in the reductive hydrolysis, structures were proposed in which more than one methylene bridge connected particular nuclei.



I

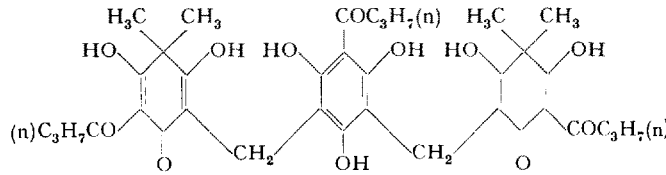


II



III IV

We suggest the alternative structure V for filixic acid.



V

This indicates a molecular formula $C_{36}H_{44}O_{12}$ (required: C, 64·6; H, 6·63; O, 28·71) which agrees well with our experimental results (found: C, 64·6; H, 6·50; O, 29·00) and those of BOEHM, but cannot be distinguished with certainty by this means from the formulae $C_{35}H_{40}O_{12}$ (required: C, 64·4; H, 6·14; O, 29·46) proposed by BOEHM. On the basis of the structure V the formation of 1:3:5-trimethylphloroglucinol is to be attributed to a disproportionation reaction[2] similar to that which leads to the formation of 1:3:5-trimethylphloroglucinol from flavaspidic acid[3]. Similarly, it has been shown that albaspidin may be formed from flavaspidic acid by disproportionation in mild alkaline conditions[3]. This provides an explanation for the formation of albaspidin from filixic acid that does not require that the two butanoylfilicinic acid units in filixic acid should be in adjacent positions.

[1] R. BOEHM, Liebigs Ann. Chem. *318*, 253 (1901).
[2] A. J. BIRCH, J. chem. Soc. *1951*, 3026.
[3] A. MCGOOKIN, A. ROBERTSON, and T. H. SIMPSON, J. chem. Soc. *1953*, 1828.

The ultraviolet absorption spectrum of filixic acid is in agreement with structure V. In ethanol it has maxima at 228 mμ (ε 41,000) and 288 mμ (ε 29,000) which are typical of enolised 2-acyl*cyclo*hexane-1:3-diones[4]. In connection with studies on the constitution of aspidin and flavaspidic acid AEBI[5] has shown that the extinction values of these compounds may be arrived at by addition of the extinction values of the component nuclei insulated by methylene groups. The addition of the extinction values at the absorption maxima of two butanoylfilicinic acid nuclei (2 × 12,510) and one phlorobutyrophenone (ε 13,000) in the region of 228 mμ gives a value of 38,120 which is in reasonable agreement with the observed value. Similarly, the calculated value at the higher wavelength maximum is 27,210.

Filixic acid does not give a coloration with GIBBS 2:6-dichloroquinonechloroimide reagent[6]. This makes suggest substitution of unlikely alternative structures for filixic acid in which there are unsubstituted positions *para* to phenolic hydroxyl groups.

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Department of Chemistry, University College of Swansea (Wales), April 16, 1957.

Zusammenfassung

Es wird die Vermutung ausgesprochen, dass Filixsäure, ein Inhaltsstoff von Farnwurzeln, die Konstitutionsformel (V) hat.

[4] W. R. CHAN and C. H. HASSALL, J. chem. Soc. *1956*, 3495.
[5] A. AEBI, Helv. chim. Acta *39*, 153 (1956).
[6] H. D. GIBBS, J. biol. Chem. *72*, 649 (1927).
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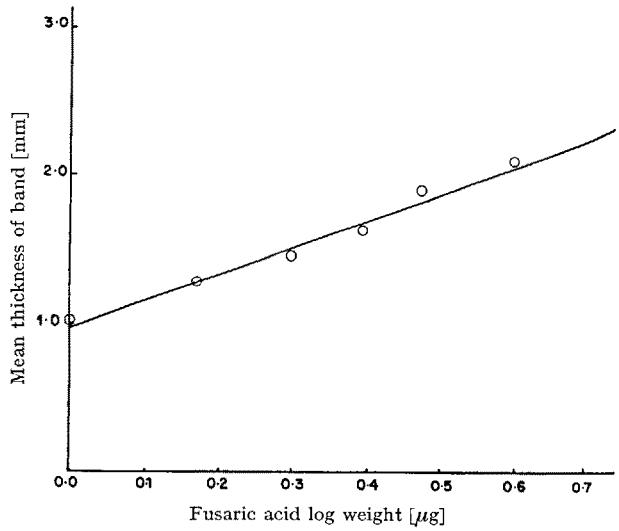
Chromatographic Detection and Estimation of Fusaric Acid

Fusaric acid was first isolated by GÄUMANN and his school of workers[1] from cultures of *Fusarium lycopersici* Sacc. and has since been known to be produced by several Fusaria. The presence of this toxin *in vivo* in wilt-infected cotton plants was reported by us earlier[2] and established to be the *vivo*-toxin in the *Fusarium* wilt of cotton. ZAHNER[3] reported the chromatographic detection and bio-assay of fusaric acid; and KALYANASUNDARAM[4], in this laboratory, developed the agar-cup technique for its assay using a soil bacterium. In view of the considerable difficulty in obtaining sharp demarcation of the fusaric acid band separated chromatographically, possibly owing to the poor ionization of the acid, we have earlier indicated the advantages of separating and identifying this toxin as its copper chelate[2]. In the present communication the detection and quantitative estimation of fusaric acid is described with the technique of paper disk chromatography developed by one of us[5]. It was considered desirable to adapt the area method developed by FISHER *et al.*[6] in preference to elution methods which have practical limitations in the small chromatograms especially when complexes with close Rf values are present.

The following amounts (as aqueous solution) of fusaric acid contained in 0·75 μl were spotted in the centre of circular filter papers (7·4 cm diameter) followed by 4 μg of copper as $CuSO_4$ (5 mg/ml): 1·0; 1·5; 2·0; 2·5; 3·0 and 4 μg. The papers were air-dried and irrigated as indicated elsewhere[5] controlling the period of irrigation at 95 min. The solvent used was *N*-butanol-acetic acid-water (4:1:5) and filter paper-Whatman No. 1. The irrigated chromatograms were sprayed with rubeanic acid (0·1% in acetone) and the colour of the bands intensified by exposure to ammonia vapour[7] (10 s). The developed chromatograms were cut into regular octogens tangentially in the 8 directions (± 45°), mounted between two square glass plates and sealed on two sides with paraffin wax. The thickness of the Cu-fusaric acid complex band was measured on the microscope using an ocular micrometre (low power). The stage readings were recorded between the points where the green colour appeared and disappeared. The mean thickness of the band in the 8 directions was computed (as the mean of 6 chromatograms) for each concentration (varying ± 3%) and plotted against log amount of the toxin on the abscissa. The typical standard curve obtained is shown in the Figure. It would be obvious that the mean thickness bears a linear relationship to the areas of the bands since the Rf values were consistent and reproducible and the bands quite circular. The areas of the complex bands are directly proportional to the logarithm of the amount of fusaric acid and independent of the total copper spotted when it is within reasonable limits. The quantitative estimation of fusaric acid in an unknown sample could easily be carried out by measuring the mean thickness of its Cu-chelate in the range of sensitivity and the amount read as the antilog of the abscissa. It may be added that the curve is not quite sensitive at concentrations of fusaric acid lower than 1 μg or higher than 4 μg.

Log fusaric acid – mean thickness curve *n*-butanol-HAC-water 4:1:5.



[1] E. GÄUMANN *et al.*, Phytopath. Z. *20*, 1 (1952).
[2] K. LAKSHMINARAYANAN and D. SUBRAMANIAN, Nature *176*, 697 (1955).
[3] H. ZAHNER, Phytopath. Z. *22*, 227 (1954).
[4] R. KALYANASUNDARAM, J. Indian bot. Soc. *34*, 43 (1955).
[5] K. LAKSHMINARAYANAN, Arch. Biochem. Biophys. *49*, 396 (1954).
[6] R. B. FISHER, D. S. PARSONS, and G. A. MORRISON, Nature *161*, 764 (1948).
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