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# CAPERATIC ACID FROM *USNEA ALATA*

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**Key Word Index**—*Usnea alata*; Usnaceae; Lichens; caperatic acid.

*Plant. Usnea alata. Source.* Growing on trees in La Carbonera (alt. 2500 m), State of Mérida, Venezuela. *Previous work.* None.

*Present work.* The light green coloured lichen (100 g) was air-dried, milled, and extracted for 9 hr with light petrol. The light petrol. extract gave 1·0 g of yellow crystals; TLC analysis showed the solid to consist of one compound which was shown (m.p., IR, TLC, $[\alpha]_D$) to be (+)-usnic acid. Continued evaporation of the light petrol. extract yielded a dark green oil whose TLC analysis indicated three compounds; the major component was identical to usnic acid; the other two of respectively smaller and greater $R_f$ than usnic acid were unidentified.

The plant residue was then continuously extracted with $Et_2O$ for 8 hr; white crystals (1·3 g) were collected from the solvent and recrystallized from $Me_2CO$–$H_2O$ to give norstictic acid (m.p., IR, TLC).

Evaporation of the $Et_2O$ extract gave yellow crystals which were shown (TLC, IR, NMR, MS, $[\alpha]_D$) to be a mixture of norstictic acid, stictic acid, and caperatic acid as major components with three unidentified trace components. (−)-Caperatic acid was separated from the above mixture by the following method: The solid was powdered, triturated thoroughly with $Et_2O$, and the solution extracted with sat. $NaHCO_3$ and acidifed with 19% HCl to yield 2·0 g of caperatic acid: m.p. 132–134° ($Me_2CO$); IR $\nu^{KBr}$ $cm^{-1}$: 3475, 3200–2700 (broad), 2940, 2910, 2840, 1728, 1675, 1460, 1440, 1370, 1255, 1237, 1214, 1115, 940, 730, 718. NMR spectrum (220 MHz, $D_3CCOCD_3$): 0·88$\delta$ (*t*, –Me), 1·29$\delta$ (*s*), 13–$CH_2$–), 2·67$\delta$ (*t*, 1H), 2·77$\delta$ (*d*, 1H, $J_{gem}$ = 16 Hz), 3·12$\delta$ (*d*, 1H, $J_{gem}$ = 16 Hz), 3·61$\delta$ (*s*, –OMe). No acidic protons were found. Rapid exchange between D of the acetone-$d_6$ and acidic protons of the acid had occurred. The geminal protons adjacent to one asymmetric carbon are non-equivalent and give a characteristic *AB* quartet.[1] The 13 methylene groups give a singlet with a broad base. This type of pattern is characteristic of long straight chain hydrocarbons.[2] MS, *m/e*: 384, 0·2% ($M^+$–$H_2O$); 371, 0·3% ($M^+$–OMe); 366, 0·8% ($M^+$–$2H_2O$); 320, 7%; 239, 9%; 184, 16%; 166, 17%; 152, 17%; 129, 20%; 116, 51%; 98, 16%; 71, 22%; 69, 27%; 59, 15% ($^+$OCOMe); 57, 51% ($C_4H_9^+$); 43, 100% ($C_3H_7^+$); 31, 14% ($^+$OMe).

The plant residue was then continuously extracted with $Me_2CO$ to exhaustion; the solvent was evaporated to give a yellow solid (2·5 g). TLC analysis showed three major components—norstictic acid, stictic acid, and an unidentified compound of very high $R_f$. The three compounds were separated by the following method: the yellow crystals were ground and triturated thoroughly with $Et_2O$. Evaporation of the solvent yielded 50 mg of

[1] R. H. BIBLE, JR., *Interpretation of NMR Spectra*, p. 73, Plenum Press, New York (1965).
[2] *Stadtler Standard Spectra*, 9661M (1970).

yellow crystals which were shown by TLC to be chiefly the compound of very high $R_f$. The crystals that remained after the washing with $Et_2O$ were washed with sat. $NaHCO_3$. Upon acidification of the combined aqueous washings with 19% HCl, 0·1 g of norstictic acid was recovered. The solid (1·5 g) which was insoluble in $NaHCO_3$ was identified as stictic acid (TLC, m.p., IR).

All TLC analyses were done with silica gel $HF_{254}$ using benzene–dioxane–HOAc, 90:25:4.

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# APIGENIN-6,8-DI-*C*-GLYCOSIDE FROM *PORELLA PLATYPHYLLA**

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**Key Word Index**—*Porella platyphylla*; Hepaticae; flavone-*C*-glycoside; vicenin.

The occurrence of isovitexin and saponarin in *Porella platyphylla* has been established[1,2] and a third flavone, occurring in minor amounts, has now been isolated and purified by gel filtration.

UV absorption data in MeOH with diagnositc shift reagents indicated an apigenin derivative with free phenolic hydroxyls.[3] Attempted acid hydrolysis proved the absence of hydrolyzable sugar. The proton NMR spectrum of the TMS ether showed the typical pattern of the B-ring protons of apigenin derivatives,[3] and a singlet (1H) at δ 6·38 ($CCl_4$, rel. TMS) which shifted to δ 6·53 on partial hydrolysis showed the presence of 3-H. Since no A-ring protons were observed and the sugar proton region (δ 3·1–5·0) integrated to *ca.* 14H the compound could be classified as a vicenin type pigment.

Acid treatment gave no discernible isomerisation, an indication that the sugar groups are identical. Acetylation gave a product, the elemental analyses of which are in agreement with those calculated for a fully acetylated (11 acetyls) apigenin diglucoside, but limited supply of material prevented investigation of the nature of the sugar components.

* Part XIV in the series "Chemical Studies on Bryophytes". For part XIII see L. SVENSSON and G. BENDZ, *Phytochem.* **11**, 1172 (1972).

[1] E. NILSSON, *Acta Chem. Scand.* **23**, 2910 (1969).
[2] N. A. TJUKAVKINA, V. BENEŠOVÁ and V. HEROUT, *Coll. Czech. Chem. Commun.* **35**, 1306 (1970).
[3] T. J. MABRY, K. R. MARKHAM and M. B. THOMAS, *The Systematic Identification of Flavonoids*, Springer, New York (1970).