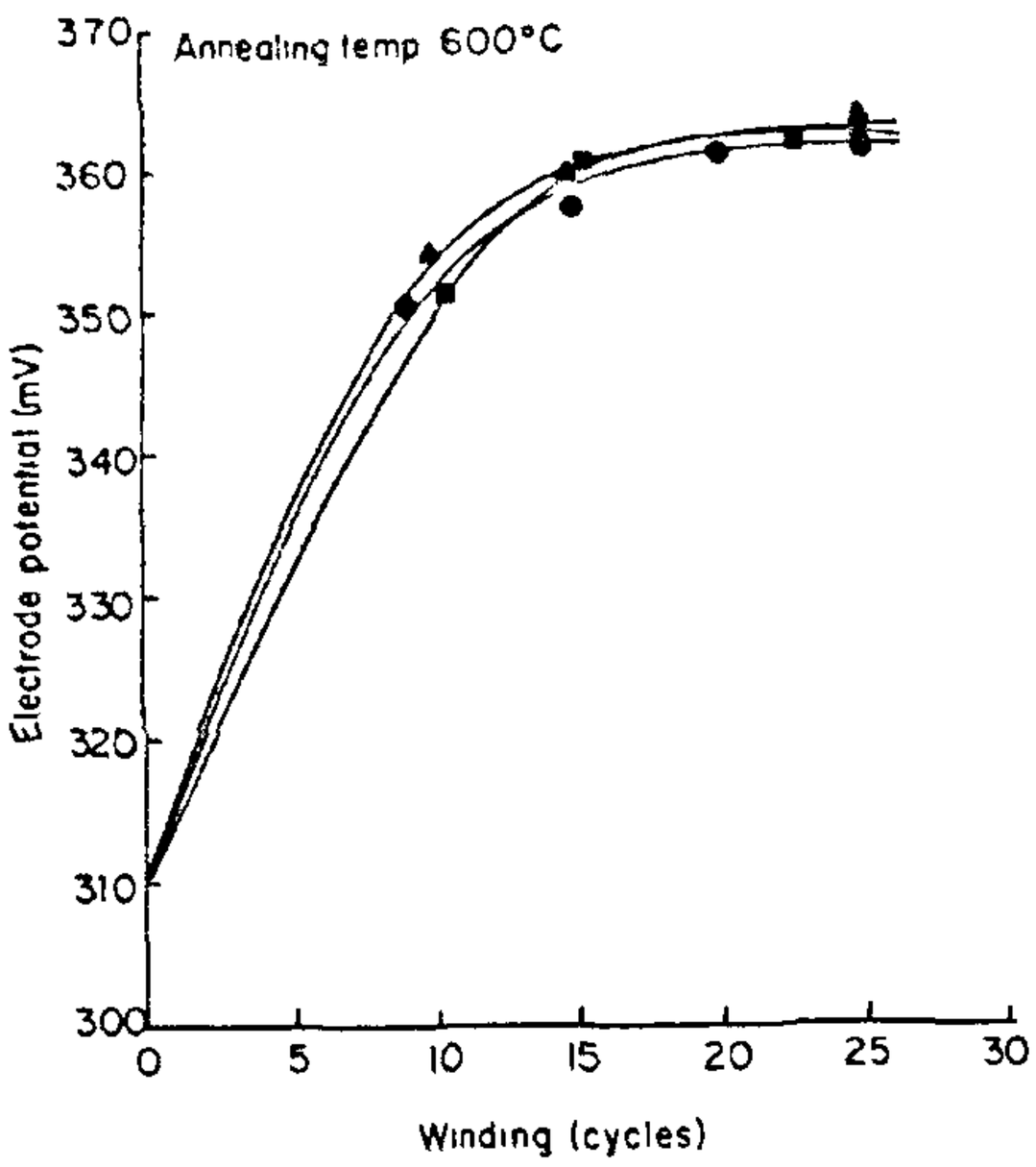

Figure 1. Typical variation in ε with the number of cycles of cold working for 3 samples annealed at 600°C.

Plane	in mV
⟨100⟩	298
⟨110⟩	392
⟨111⟩	336

Planes ⟨100⟩, ⟨111⟩ have ε values nearest to the recovered values for wire samples annealed at 290° and 425°C respectively. These must therefore be the planes dominating the surface for these samples.

For the sample annealed at 240° the value of recovered ε lies between the values for ⟨100⟩ and ⟨111⟩ planes. An empirical fit gives the fractional contributions from the two surfaces close to 2:1 other contributions shown in the last column of table 1 are calculated likewise. This is only an empirical interpretation of the observed ε values.

The data indicate that the annealed polycrystalline wires on cold-working have surfaces with some preferred crystal planes. Which of the planes shall dominate depends sharply on the annealing temperature.

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CHEMISTRY OF LICHEN PRODUCTS—PART II: SYNTHESIS AND BIOLOGICAL ACTIVITY OF SOME NEW DERIVATIVES OF PULVINIC DILACTONE

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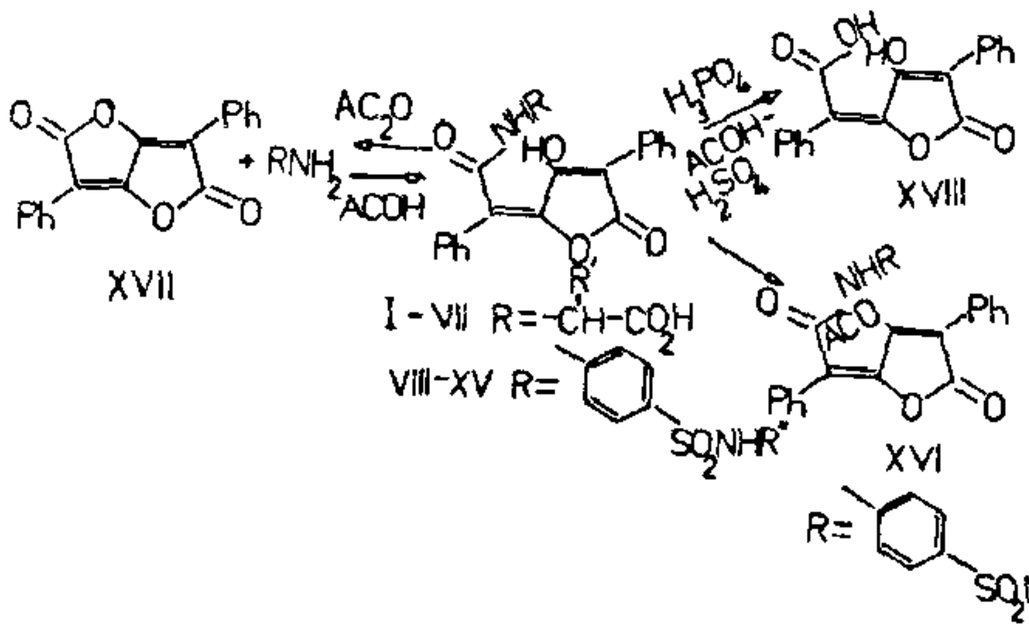
LICHEN metabolites of pulvinic acid group[1] possess the tetronic acid ring system which is also present in a number of important natural products *viz* vitamin C and the cardenolide, digitoxigenin.

With a view to synthesizing more potent biologically active compounds, various amino acids and differently substituted sulphanilamides are condensed with pulvinic dilactone[2] by refluxing in acetic acid for 4–5 hr (scheme-I). While the products derived from aminoacids yielded pulvinic dilactone on boiling with acetic anhydride for 3 hr, they gave pulvinic acid on hydrolysis using polyphosphoric acid or acetic acid-sulphuric acid mixture. Further, the enolic hydroxyl of simple sulphonamide condensation product (VIII) got esterified on refluxing in acetic acid for one hour to get its acetate (XVI).

The hydrolysis products were identified by CO TLC, superimposable IR and mixed m.p. measurements. Structures of the products (table 1) were established by the following spectral data. IR ν_{max} in cm^{-1} (I–VII): 3220–3390 (broad, OH, NH), 1760s (C=O, lactone), 1700–1710s (C=O, carboxylic acid), 1650s (C=O, amide) 1610m (aliphatic C=C).

IR ν_{max} in cm^{-1} (VIII–XV): 3200–3400 (broad, NH, OH), 1760s (C=O, lactone), 1650s (C=O, amide), 1610m (aliphatic C=C), 1350, 1160s (–SO_2–). (XVI) Acetate of (VIII): 3300 (broad, NH), 1760 (C=O, lactone), 1730 (C=O, ester), 1650 (C=O, amide), 1350 and 1160 (–SO_2–).

PMR of compound (V): In ppm, 1.9 (s, 3H, –CH_3), 2.1 (qua., 2H, –CH_2–) 2.5 (t, 2H, –CH_2–), 4.85 (qua., 1H, –CH–N–), 9.5 (broad, 1H, –CO–NH–), 10.5 (s, 1H, –CO_2H) and 12.8 (s, 1H, –OH).



Scheme-I

Compound (VIII): 6.0–6.2 (s, 2H, $-SO_2NH_2$), 7.3–8.0 (m, 14H, aromatic) 9.0 (broad, s, 1H, –CO–NH–) and 13.0 (s, 1H, enolic). Acetate of (VIII): 1.98 (s, 3H, $-COCH_3$) in addition to the above signals.

Compound IX: 2.0 (s, 3H-Me), 10.2 (s, 1H, SO_2NH–), 13.2 (s, 1H, enolic), 7.5–8.2 (m, 14H, aromatic).

Compound (X): 2.3 (s, 3H, $-CH_3$), (XI) 3.85 (s, 6H, 2OMe) in addition to the sulphanilamide product (VIII) signals.

Mass data: (V) in its spectrum showed a peak at m/z 149, corresponding to methionine, III at 103 for α-amino butyric acid), IX at 214 due to N^1-acetyl sulphanilamide and XI at 310 for N^1-(2,6-dimethoxy,4-pyrimidinyl) sulphanilamide in addition to common peaks at 290 (base peak) 261, 234, 178, 145, 117 and 89 mass values, which is the characteristic feature of pulvinic acid series[3].

Melting points were taken in open capillaries and are uncorrected. Compounds were routinely checked for their homogeneity by TLC on plates coated with silicagel-G. IR spectra were recorded in nujol mull, while the PMR spectra were recorded in either $CDCl_3$ or DMSO-d_6 using TMS as internal standard.

Antibacterial activity was studied *in vitro* using cup-plate method[4] and antifungal activity by humid chamber technique[5]. The bacteria employed were *Bacillus megatherium* (BM) and *Bacillus Pumilus* (BP) (both gram-positive) and *Escherichia coli* (EC) and *Pseudomonas ovallis* (PO) (gram-negative). The two

Table 1 *Characterization data of different pulvinamides*

Compound	Amine	m.p.°C	Yield	Mol. Formula	Found (Calcd.) % C	H	N
I	L-phenylglycine	210	70	$C_{26}H_{19}O_6N$	70.12(70.74)	4.1(4.30)	3.1(3.17)
II	L-Valine	188	65	$C_{23}H_{21}O_6N$	66.5(67.8)	4.9(5.15)	3.39(3.43)
III	α-Amino n-butyric acid	195	60	$C_{22}H_{19}O_6N$	65.7(67.1)	4.5(4.8)	3.5(3.56)
IV	Arginine	202	72	$C_{24}H_{24}O_6N_4$	61.5(62.0)	4.9(5.1)	12.01(12.06)
V	Methionine	152	80	$C_{23}H_{21}O_6NS$	62.0(62.8)	4.5(4.7)	3.05(3.18)
VI	Threonine	135	60	$C_{22}H_{19}O_7N$	64.1(64.5)	4.2(4.6)	3.4(3.42)
VII	Ornithine	145	62	$C_{23}H_{22}O_6N_2$	65.1(65.6)	5.0(5.2)	6.57(6.6)
VIII	Sulphanilamide	195	80	$C_{24}H_{18}O_6N_2S$	61.5(62.5)	3.5(3.8)	6.05(6.06)
IX	N^1-Acetyl "	205	75	$C_{26}H_{20}O_7N_2S$	60.5(61.9)	3.4(3.9)	5.5(5.55)
X	N^1-(5-methyl-3-isoxazolyl) "	244	75	$C_{28}H_{21}O_7N_3S$	61.5(61.8)	3.17(3.8)	7.65(7.73)
XI	N^1-(2,6-dimethoxy 4-pyrimidinyl) "	238	80	$C_{30}H_{24}O_8N_4S$	60.0(60.0)	3.9(4.0)	9.28(9.33)
XII	N^1-Amidino "	242	70	$C_{25}H_{20}O_6N_4S$	58.5(59.5)	3.5(3.96)	11.23(11.11)
XIII	N^1-(1-phenyl, pyrazole-5-yl) "	248	80	$C_{33}H_{24}O_6N_4S$	65.0(65.5)	3.8(3.95)	9.2(9.27)
XIV	N^1-(5-methyl-1,3,4-thiadiazolo-2-yl)	270	80	$C_{27}H_{20}O_6N_4S_2$	57.5(57.8)	3.2(3.57)	10.0(10.0)
XV	N^1-(2-pyrimidinyl) "	235	70	$C_{28}H_{20}O_6N_4S$	61.7(62.2)	3.2(3.7)	10.1(10.37)
XVI	Acetate of VIII	145	85	$C_{26}H_{20}O_7N_2S$	61.7(61.9)	3.7(3.9)	5.4(5.55)

Solvents for crystallisation: I to IV acetic acid, V benzene, VI chloroform, VII acetone, XVI acetic acid
VIII to XV could not be recrystallised owing to their poor solubility in a number of solvents. However, they are homogeneous on TLC.

Table 2 *Biological activity results*

Compound	Anti fungal activity D. *Rostrata* A	*B* (C)	F. *Oxysporum* A	*B* (C)	Antibacterial activity Diameter of zone inhibition* BM	BP	EC	PO**
I	250	2.08 (1.15)	200	2.05 (1.16)	20	20	20	20
II	150	2 19 (1.09)	150	2.05 (1.08)	10	10	8	10
III	250	2.39 (1.0)	250	2.29 (1.04)	14	14	14	14
IV	150	2.20 (1.09)	150	2.18 (1.09)	20	22	14	20
V	150	2.23 (1.07)	150	2.18 (1.09)	10	10	8	8
VIII	—	—	—	—	8	22	6	6
IX	—	—	—	—	14	22	6	6
X	140	2.06 (1.16)	140	2.14 (1.11)	20	22	6	6
XI	120	2.08 (1.15)	120	2.05 (1.16)	20	22	6	6
XII	160	2.20 (1.08)	160	2.20 (1.08)	14	22	6	6
XIII	160	2.19 (1.09)	160	2.20 (1.08)	—	—	—	—
XIV	120	2.09 (1.15)	120	2.08 (1.15)	—	—	—	—

Stock solutions used for biological screening: Antifungal, 1 mg/1 ml in acetone; Antibacterial, 10 mg/1 ml, VIII to XII in propylene glycol, I to V in dioxan (A) Concentration in ppm for 50 % inhibition (B) log Ed_{50} values (C) Relative toxicity.

* Values include the diameter of the cup (6 mm) also.

** See the discussion part.

photopathogenic fungi used for the purpose were *Drechslera rostrata* and *Fusarium oxysporum*. Biological screening results are given in table 2.

The compounds (VIII–XII) prepared by condensing sulphanilamides with pulvinic dilactone exhibited strong antibacterial activity which is comparable to the activity of their respective pure sulpha drugs yet only against gram positive organisms, similar to the action of most of the lichen metabolites. But the products obtained by the condensation of aminoacids are equally active against the both types of organisms. Hence the activity appears to depend on the structure of amine part of these pulvinamides and pulvinyl group does not seem to have any control over it.

In general the aminoacid derivatives are more fungitoxic than their sulpha counterparts. Though sulpha drugs as such have no antifungal activity, their products exhibited moderate to strong activity against the organisms screened.

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