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X-Ray Diffractometric Study of α- and β-Flavaspidic Acids

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The crystal structures of α- and β-flavaspidic acids have been determined. α-Flavaspidic acid appears to be orthorhombic and the unit cell dimensions are $a=14.60$, $b=25.53$, and $c=16.40$ Å. β-Flavaspidic acid is monoclinic, $a=17.11$, $b=22.16$, and $c=19.39$ Å, $\beta=89°20'$.

Flavaspidic acid (*1*), one of the major constituents of *Dryopteris* ferns, is the methylene-linked dimer of butyrylfilicinic acid and methylbutyrylphloroglucinol. It appears in two modifications. Recrystallization from alcohol yields the α-form which melts at 92°C (Fig. 1). On continuous heating it crys-

Fig. 1. α-Flavaspidic acid. (Magnification ×150.)

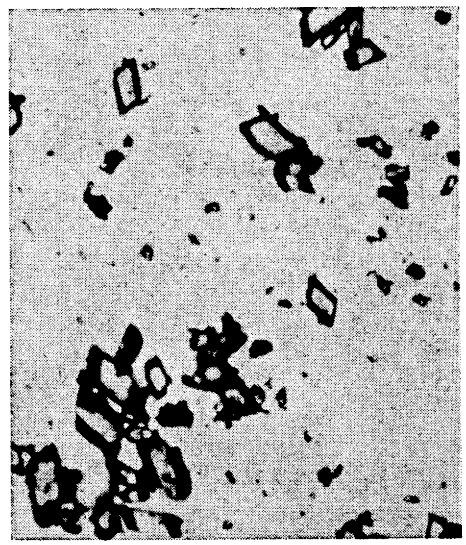
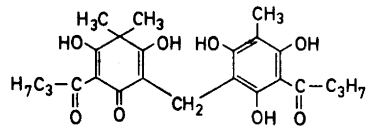


Fig. 2. β-Flavaspidic acid. (Magnification ×150.)

tallizes and melts again at 156°C. The latter melting point is that of the β-flavaspidic acid, which can be obtained by recrystallization, *e.g.* from benzene (Fig. 2).



(*I*)

Boehm [1] supposed the two forms of flavaspidic acid to be tautomers, the lower melting being the enolic one. About fifty years later Riedl [2] suggested that crystal methanol, rather than tautomerism, were the cause of the double melting point of α-flavaspidic acid, but this opinion was soon abandoned.[3] However, on röntgenographic examination a perfect identity of the two modifications in powder form was recorded[4], and this again supported the opinion that the keto-enol tautomerism were not the correct interpretation of the two forms. Finally, the tautomerism of flavaspidic acid was settled by Aho [5] in a comparative spectral study and determination of the keto-enol equilibrium in different solvents.

Table 1. Observed and calculated structure factors for α-flavaspidic acid.

2θ	I	$\sin^2\theta_{obs}$	$h\,k\,l$	$\sin^2\theta_{calc}$
6.05	vvs	0.00278	1 0 0	0.00278
6.90	vw	0.00362	0 2 0	0.00362
10.36	vs	0.00815	0 3 0	0.00815
10.78	vs	0.00882	0 0 2	0.00884
12.11	vs	0.01113	2 0 0	0.01112
13.69	m	0.01420	2 1 1	0.01424
14.90	m	0.01681	0 4 1	0.01670
15.98	s	0.01932	2 3 0	0.01927
19.05	m	0.02738	1 5 1	0.02764
20.55	vvs	0.03182	2 1 3	0.03192
20.97	s	0.03312	3 2 0	0.03317
21.70	m	0.03543	0 0 4	0.03536
23.72	s	0.04224	2 5 2	0.04201
24.45	w	0.04484	3 0 3	0.04491
24.85	m	0.04629	2 0 4	0.04648
27.35	m	0.05589	1 7 2	0.05601
28.40	m	0.06018	3 0 4	0.06038
29.37	m	0.06426	4 0 3	0.06437
30.05	m	0.06721	2 1 5	0.06728
34.45	vw	0.08769	0 3 6	0.08771
35.19	w	0.09138	2 1 6	0.09159
37.43	m	0.10295	6 1 1	0.10320
38.49	w	0.10864	6 0 2	0.10892
39.43	vw	0.11380	5 9 0	0.11389
41.93	w	0.12802	5 2 5	0.12837
48.35	w	0.16771	3 1 8	0.16737

We now present an X-ray diffractometric study of the two forms of flavaspidic acid.

The following conclusions could be deduced from the diffraction data.

α-Flavaspidic acid appeared to be orthorhombic as calculated from the data in Table 1.

$a = 14.60$ Å, $b = 25.53$ Å, $c = 16.40$ Å.

β-Flavaspidic acid, on the other hand, appeared to be monoclinic (Table 2).

$a = 17.11$ Å, $b = 22.16$ Å, $c = 19.39$ Å, $\beta = 89°20'$.

α-Flavaspidic acid, which melted at 92°C, recrystallized when kept in a thermostate at 110°C. The X-ray diffraction diagram obtained from the recrystallized acid was identical with the one obtained earlier for the β-flavaspidic acid.

Table 2. Observed and calculated structure factors for β-flavaspidic acid.

2θ	I	$\sin^2\theta_{obs}$	$h\,k\,l$	$\sin^2\theta_{calc}$
7.99	vs	0.00485	0 2 0	0.00485
9.52	vw	0.00689	1 2 0	0.00688
10.35	m	0.00814	2 0 0	0.00814
11.49	vs	0.01002	2 0 1	0.00985
12.04	s	0.01100	0 3 0	0.01092
12.83	m	0.01248	0 3 1	0.01250
13.69	vs	0.01420	0 0 3	0.01425
15.60	m	0.01842	3 0 0	0.01832
16.30	vs	0.02010	3 0 1	0.02011
16.88	m	0.02154	1 4 0	0.02144
17.83	m	0.02402	2 1 3	0.02402
20.09	m	0.03042	0 5 0	0.03033
21.40	m	0.03447	4 0 1	0.03442
21.90	m	0.03608	3 3 2	0.03599
22.95	vvs	0.03958	0 0 5	0.03958
24.10	m	0.04358	0 6 0	0.04367
24.95	m	0.04666	1 4 4	0.04649
25.89	m	0.05018	−3 5 1	0.05032
26.30	vs	0.05176	1 6 2	0.05187
27.60	m	0.05690	0 0 6	0.05699
28.65	w	0.06122	0 7 1	0.06102
29.10	vw	0.06311	−5 3 1	0.06303
30.40	m	0.06874	5 3 2	0.06883
30.90	m	0.07097	5 2 3	0.07103
31.59	m	0.07409	2 7 2	0.07419
32.61	m	0.07882	1 4 6	0.07885
33.30	vw	0.08210	−4 6 2	0.08200
34.10	m	0.08597	−1 8 2	0.08585
35.50	m	0.09294	4 4 5	0.09295
36.10	vw	0.09601	3 4 6	0.09596
37.30	vw	0.10226	3 2 7	0.10221
38.47	m	0.10853	3 3 7	0.10828
39.72	m	0.11541	7 0 3	0.11544
42.00	vw	0.12843	5 8 0	0.12851
43.60	w	0.13791	7 3 4	0.13793
44.69	m	0.14454	7 6 1	0.14448
45.60	vw	0.15017	5 9 1	0.15036
46.95	w	0.15868	0 0 10	0.15830
48.10	m	0.16608	9 1 0	0.16605
48.80	vw	0.17066	9 2 1	0.17064

EXPERIMENTAL

Flavaspidic acid was obtained from *Dryopteris assimilis* S. Walker rhizomes by the isolation method earlier described.[6] A batch of crude flavaspidic acid was divided into two samples which were separately purified by recrystallizations from methanol and benzene, respectively, until the melting points of pure α- and β-flavaspidic acids were obtained.

X-Ray diffraction data. In the diffractometric studies a Philips X-ray diffractometer (flat plate powder specimen) and Cu$K\alpha$ radiation were used. The speed of the goniometer was $2\theta = \frac{1}{8}^{\circ}$/min. The diffractometric results are presented in Tables 1 and 2. The lines in the tables were corrected with the known lines of sodium chloride.

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