

*Studies of the Structure of Bergenin**

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Two reports on the structure of bergenin were published recently by J. Evelyn Hay et al.¹⁾ and by Posternak et al.²⁾. We also wish to report here our results on the structure of bergenin (I) from the bark of *Corylopsis Spicata*³⁾.

The periodate oxidation of di-*O*-methylbergenin (II) gave 5,6,7-trimethoxyisocoumarin-3-aldehyde (III). By careful catalytic hydrogenation of III, 3-hydroxy-methyl-5,6,7-trimethoxyisocoumarin (IV)

* The paper was read at Annual Meeting of Chemical Society of Japan, April 5, 1958.

1) J. E. Evelyn Hay et al., *J. Chem. Soc.*, 1958, 2231.

2) Posternak et al., *Helv. Chim. Acta*, 41, 1159 (1958).

3) Hattori, *Acta Phytochim.*, (Japan), 4, 327 (1929).

(its 3-acetoxymethyl derivative (V)), 3-methyl-5,6,7-trimethoxyisocoumarin (VI) and 3-methyl-5,6,7-trimethoxy-3,4-dihydroisocoumarin (VII) were isolated through three steps.

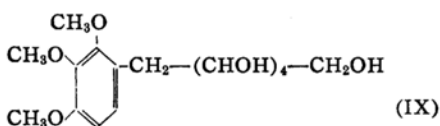
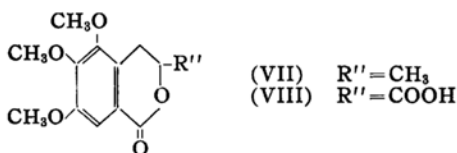
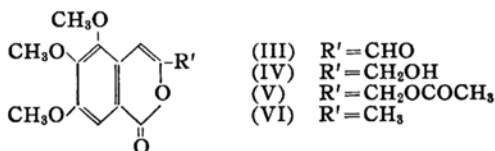
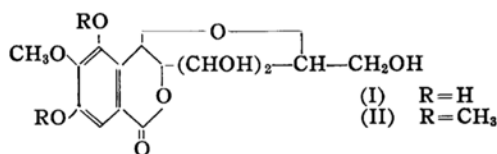
The alkaline treatment of III gave 5,6,7-trimethoxy-3,4-dihydroisocoumarin-3-carboxylic acid (VIII), i. e., an intermolecular Cannizzaro reaction was observed. The values of U. V. spectrum of these compound are given in Tables I and II.

TABLE I
U. V. ABSORPTION OF BERGENIN AND ITS
DERIVATIVES
(λ_{\max} in $m\mu$)

Group 1			Group 2		
Compound	λ_{\max}	$\log \epsilon$	Compound	λ_{\max}	$\log \epsilon$
I	275	3.903	III	335	3.856
	220	4.426		245	4.600
II	268	3.914	IV	338	3.726
	220	4.482		247	4.680
VII	305	3.485	V	335	3.705
	265	3.962		247	4.684
	220	4.415	VI	340	3.658
VIII	303	3.397		245	4.655
	265	3.874			
	220	4.388			

TABLE II
CARBONYL STRETCHING FREQUENCIES IN I. R.
SPECTRA OF BERGENIN AND ITS DERIVATIVES

Compound	ν (cm^{-1})
I	1703
II	1721, 1711
Penta- <i>O</i> -acetylbergenin	1775, 1733



From the results shown in Table I, we conclude that bergenin and di-*O*-methylbergenin have dihydroisocoumarin-ring, but not isocoumarin-ring (the absence of $330 m\mu$ absorption). The results also agreed with those in Table II, i. e., I. R. spectrum of 3-methyl-3,4-dihydroisocoumarin (1716 cm^{-1}) indicated the identical structure with that of bergenin and of di-*O*-methylbergenin.

The catalytic reduction of II, by using Raney catalyst (at 200° , 100 atm.) resulted in obtaining 6-(2,3,4-trimethoxyphenyl)-1,2,3,4,5-heptahydroxyhexane IX, being accompanied by both decarboxylation and hydrogenation. The products was stable to Fehling's solution. The constitution of IX was also confirmed by the oxidation with sodium metaperiodate. In the case that 4 moles of this reagent were consumed, oxidation product was isolated to be prove as 2,3,4-trimethoxy phenylacetaldehyde 2,4-dinitrophenyl hydrazone.

The alkaline hydrogen peroxide oxidation of I gave arabinose (as 2,4-dinitrophenylhydrazone). II was found to be also stable to Fehling's solution. Deducing from the above-mentioned experimental results, bergenin is concluded to be represented by the formula I.

TABLE III
ANALYSES

No.	Formula, m. p.	Found.		Calcd.	
		C%	H%	C%	H%
III	$\text{C}_{13}\text{H}_{12}\text{O}_8$ m. p. $160\sim 161^\circ$	58.85	4.53	59.09	4.58
IV	$\text{C}_{13}\text{H}_{14}\text{O}_8$ m. p. $141\sim 142^\circ$	58.88	5.51	58.64	5.30
V	$\text{C}_{15}\text{H}_{16}\text{O}_7$ m. p. $93\sim 94^\circ$	58.42	5.06	58.44	5.23
VI	$\text{C}_{13}\text{H}_{14}\text{O}_8$ m. p. $84\sim 86^\circ$	62.57	5.71	62.39	5.64
VII	$\text{C}_{13}\text{H}_{16}\text{O}_8$ m. p. $67\sim 69^\circ$	61.60	6.10	61.89	6.39
VIII	$\text{C}_{13}\text{H}_{14}\text{O}_7$ m. p. $157\sim 158^\circ$	55.33	5.08	55.32	5.00
IX	$\text{C}_{15}\text{H}_{24}\text{O}_8$ m. p. $182\sim 183^\circ$	54.87	6.51	54.21	7.28

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4) J. Blair et al., *J. Chem. Soc.*, 1955, 2871.