

Lucernol and Sativol, Two New Coumestans from Alfalfa (*Medicago sativa*)

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The structures of two new naturally occurring phenolic compounds have been established. Characterization of 6,7,12-trihydroxycoumestan ($C_{15}H_8O_6$) was accomplished by fusion, proton magnetic resonance, and ultraviolet spectral studies. Characterization of 8,12-dihydroxy-7-methoxycoumestan ($C_{16}H_{10}O_6$) was accomplished by systematic degradation to 4-methoxy-2-(2',3',4'-trimethoxy benzoyl)-benzaldehyde. The methoxyl group was located by ultraviolet spectral studies and confirmed by PMR spectroscopy through a comparison of the ether-acetate shifts of the aromatic protons.

THE presence in plants of compounds having the coumestan ring pattern was first reported by Govindachari, Nagarajan, and Pai (8) in 1956. From *Wedelia calendulacea*, they isolated 5,11,12-trihydroxy-7-methoxycoumestan (5), to which they assigned the name Wedelolactone. Since then, six additional compounds having this basic ring structure have been isolated from widely different plants: coumestrol (7) from *Trifolium repens*, crosnin (7) from *Pachyrhizus erosus*, psoralidin (4) from *Psoralea corylifolia*, trifoliol (12) from *Trifolium repens*, and medicagol (13) and 4'-O-methylcoumestrol (3) from *Medicago sativa*.

In our continuing investigation of phenolic compounds from forages, two new coumestans from alfalfa have been characterized, and the trivial names sativol and lucernol are proposed.

Experimental

Isolation. Lucernol and sativol were isolated from an acetone extract of dehydrated alfalfa meal by a series of countercurrent distributions. The solvent systems employed and the details of their isolation have been presented (2).

Purification. Sativol (2, compound VII) was purified by recrystallization from methanol (m.p. 303° C.).

Calculated for $C_{16}H_{10}O_6$: C, 64.4; H, 3.38; OCH_3 , 10.4. Found: C, 64.3; H, 3.46; OCH_3 , 10.1.

Lucernol (2, compound VI) was purified by recrystallization from dimethylsulfoxide (m.p. >350° C.).

Calculated for $C_{15}H_8O_6$: C, 63.4; H, 2.84; OCH_3 , 0.0. Found: C, 62.8; H, 3.20; OCH_3 , 0.0.

Alkaline Fusion. Sativol (25 mg.) or lucernol (25 mg.) was fused with ground potassium hydroxide for 1 minute. After cooling, the mixture was neutralized and the fusion products were extracted with ether. Aliquots of the ether extract were spotted on Whatman No. 1 paper with and without known compounds. Following two-dimensional development in chloroform-acetic acid-

water (2:1:10, organic phase) and 20% potassium chloride, the chromatograms were observed under ultraviolet light before and after treatment with ammonia and then in visible light after spraying with diazotized sulfanilic acid. Spots were detected corresponding to resorcinol and hydroxyhydroquinone for lucernol and resorcinol, β -resorcylic acid, pyrogallol, and pyrogallol carboxylic acid for sativol.

Derivatives of Lucernol. ACETATE (I, $R_1 = R_2 = R_4 = CH_3CO$, $R_3 = H$). Lucernol (100 mg.), anhydrous sodium acetate (200 mg.), and acetic anhydride (2.0 ml.) were heated at reflux for 3 minutes, cooled, and poured into cold water, giving 110 mg. of white needles. An analytical sample (m.p. 253-54° C.) was prepared by recrystallization from acetone.

Calculated for $C_{21}H_{14}O_9$: C, 61.5; H, 3.44; CH_3CO , 31.5. Found: C, 61.4; H, 3.60; CH_3CO , 33.0.

TRIMETHYL ETHER (I, $R_1 = R_2 = R_4 = OCH_3$, $R_3 = H$). Lucernol (100 mg.), potassium carbonate (250 mg.), dimethyl sulfate (1.0 ml.), and dry acetone (50 ml.) were heated at reflux for 24 hours. The reaction mixture was cooled and filtered, and the solids were washed with water. Recrystallization from methanol gave a white solid (102 mg.) (m.p. 255° C.).

Calculated for $C_{18}H_{14}O_6$: C, 66.3; H, 4.29; OCH_3 , 28.8. Found: C, 66.2; H, 4.46; OCH_3 , 28.5.

Derivatives of Sativol. ACETATE (I, $R_1 = H$, $R_2 = OCH_3$, $R_3 = R_4 = CH_3CO$). Sativol (100 mg.), anhydrous sodium acetate (200 mg.), and acetic anhydride (2.0 ml.) were heated at reflux for 3 minutes, cooled, and poured into cold water. The water mixture was filtered, giving 120 mg. of a white solid. An analytical sample (m.p. 256-57° C.) was prepared by recrystallization from acetone.

Calculated for $C_{20}H_{14}O_8$: C, 62.8; H, 3.69; CH_3CO , 22.1; OCH_3 , 8.12. Found: C, 62.8; H, 3.71; CH_3CO , 22.9; OCH_3 , 8.03.

DIMETHYL ETHER (I, $R_1 = H$, $R_2 = R_3 = R_4 = OCH_3$). Sativol (1.0 gram), potassium carbonate (2.0 grams), di-

methyl sulfate (5.0 ml.), and dry acetone (150 ml.) were heated at reflux for 10 hours. The reaction mixture was cooled and filtered, and the solids were washed with water. Recrystallization from methanol gave white needles (0.94 gram) (m.p. 209-10° C.).

Calculated for $C_{18}H_{14}O_6$: C, 66.3; H, 4.29; OCH_3 , 28.8. Found: C, 66.3; H, 4.35; OCH_3 , 28.5.

TETRAMETHYL ETHER-METHYL ESTER (II, $R = CH_3$). Sativol (2.0 grams), potassium carbonate (10.0 grams), dimethyl sulfate (10 ml.), and dry acetone (300 ml.) were heated at reflux for 6½ hours. The mixture was maintained basic during the course of the reaction by addition of 10% potassium hydroxide in methanol. The reaction mixture was taken to dryness and partitioned between chloroform and water (100 ml. each). After removal of the chloroform, the crude oil was crystallized from methanol to give 2.11 grams of a white solid. An analytical sample (m.p. 107.5-08° C.) was prepared by recrystallization from methanol.

Calculated for $C_{20}H_{20}O_7$: C, 64.5; H, 5.38; OCH_3 , 41.7. Found: C, 64.6; H, 5.36; OCH_3 , 41.7.

O-METHOXYCINNAMIC ACID (II, $R = H$). The above ester (2.1 grams) was heated at reflux in 50 ml. of 10% potassium hydroxide in methanol for 4½ hours. Dilution with water and acidification gave a white solid. The acid was recrystallized from methanol-water to give 1.78 grams of clear plates (m.p. 222.5° C.).

Calculated for $C_{19}H_{18}O_7$: C, 63.7; H, 5.04; OCH_3 , 34.7. Found: C, 63.7; H, 5.18; OCH_3 , 34.5.

2-(2',3',4'-TRIMETHOXYPHENYL)-6-METHOXYBENZOFURAN (III). The above acid (1.68 grams) was mixed with an equal amount of powdered soft glass and heated under N_2 at 280-5° C. for 20 minutes. The reaction mixture was cooled, dissolved in methanol, filtered, and concentrated to 20 ml. Upon cooling, 1.37 grams of a brown solid separated. The material was purified by countercurrent distribution in a robot-operated, 100-tube (20 ml. per tube) instrument with Skellysolve B-

Table I. Ultraviolet Spectra of Coumestans

Compound	Max M_{μ}		NaAc/ boric acid
	Neutral	NaAc	
Coumestrol ^a	343	362	
	304	312	
	244	243	
Trifoliol	348	372	
	309	312	
	268	270	
Medicagol	362(s) ^b	380(s)	
	348	362	
	308	318	
	245	247	
7-O-Methylcoumestrol ^a	342	342	
	303	303	
	243	243	
7-O-Benzylcoumestrol ^a	343	343	
	303	304	
	244	244	
Sativol	342	342	
	305	305	
	241	241	
Lucernol	372(s)	392(s)	378
	355	372	362(s)
	310	315	312
	232	272	238
7,11,12-Trihydroxycoumestan	352	358	372
	309	309	316
	248	250	295 255

^a Taken from (10).^b Slope.

methanol-acetone-water (100:25:15:1) as the developing system. The first 200 transfers off the instrument were free of any organic matter and discarded. The next 90 transfers were combined and taken to dryness, giving 0.90 gram

of a white solid. Recrystallization from methanol gave an analytical sample (m.p. 84.5–85° C.).

Calculated for $C_{18}H_{18}O_5$: C, 68.8; H, 5.74; OCH_3 , 39.5. Found: C, 68.8; H, 5.71; OCH_3 , 39.6.

OZONOLYSIS OF BENZOFURAN (III). A solution of the benzofuran (150 mg.) in methylene chloride (25 ml.) was cooled to approximately -65° C. in a dry ice-methanol bath, and a gentle stream of 2% ozone in oxygen was passed through the mixture for 2½ hours. Triethyl phosphite (0.2 ml.) was added, and the reaction mixture was brought to room temperature and extracted with dilute alkali, which was then acidified and re-extracted with ether. The ether solution was concentrated to an oil, which was crystallized from Skellysolve B, giving 10 mg. of a white solid (m.p. 101° C.). An authentic sample of 2,3,4-trimethoxybenzoic acid (9) did not depress the melting point of the isolated compound. The ultraviolet and infrared spectra of the isolated crystals and the authentic acid were identical.

The methylene chloride solution was concentrated to an amber gum, which crystallized from methanol-water, giving 84.2 mg. of the intermediate aldehyde (IV). An analytical sample was prepared from methanol-water (m.p. 100–01° C.).

Calculated for $C_{18}H_{18}O_7$: C, 62.4; H, 5.20; OCH_3 , 35.8. Found: C, 62.3; H, 5.43; OCH_3 , 35.9.

Synthesis of 4-Methoxy-2-(2',3',4'-trimethoxybenzoyl)-benzaldehyde (IV). A solution of 2,3,4-trimethoxybenzoic acid (200 mg.) in methylene chloride (5 ml.) containing 0.8 ml. of thionyl chloride was refluxed for 2½ hours, then taken to dryness in vacuo. The

crude acid chloride, methylene chloride (5 ml.), pyridine (0.3 ml.), and 2-hydroxy-4-methoxybenzaldehyde (125 mg.) were refluxed for 4½ hours. The reaction mixture was washed with alkali and concentrated to give 290 mg. of an amber sirup. The material was purified by chromatography on a silica gel column (2.5 × 15 cm.). Increasing amounts of ether in Skellysolve B were used as eluent. The fraction that eluted with 40% ether in Skellysolve B was taken to dryness and crystallized from methanol-water, giving 110 mg. of a white solid (m.p. 101° C.).

Calculated for $C_{18}H_{18}O_7$: C, 62.4; H, 5.20; OCH_3 , 35.8. Found: C, 62.3; H, 5.36; OCH_3 , 35.5.

The infrared spectrum, R_f values, and mixed melting point of the synthetic aldehyde were identical with those of the aldehyde (IV) from the natural product.

Proton Magnetic Resonance Study. The acetates of the compounds used in this study were very insoluble in organic solvents normally used in PMR work and decomposed in D_7 -dimethylformamide. 1,1,2,2-Tetrachloroethane (TCE) was used because it is inert, and at 120° C. dissolved sufficient sample to give reasonably good spectra. In compounds sufficiently soluble in both chloroform and TCE, no differential solvent shifts were observed. In some cases it was necessary to enhance the sensitivity by a factor of 5 by time-averaging with a 1024-channel pulse analyzer.

Results and Discussion

The similarity of the ultraviolet and PMR spectra of the two compounds to

Table II. Shielding of Ring Protons^a for Acetate and Methoxyl Derivatives of Coumestans

Compounds	H-5	H-6	H-8	H-10	H-11	H-13
1. Coumestrol dimethyl ether (7,12-dimethoxycoumestan)	2.17	^b	^b	2.09	^b	^b
2. Coumestrol diacetate	2.05	2.82	2.74	1.97	2.87	2.52
1 minus 2	-0.12 (M) ^c			-0.12 (M)		
3. 4'-O-Methylcoumestrol acetate (7-acetyl-12-methoxycoumestan)	2.07	2.89	2.77	2.07	3.00	2.87
1 minus 3	-0.10 (M)					
3 minus 2					-0.13 (O)	-0.35 (O)
4. Trifoliol dimethyl ether (7,10,12-trimethoxycoumestan)	2.24	3.27	3.09	^d	3.27	3.55
5. Trifoliol diacetate (7,10-diacetyl-12-methoxycoumestan)	2.12	2.87	2.79	^d	2.97	3.27
4 minus 5	-0.12 (M)	-0.40 (O)	-0.30 (O)		-0.30 (O)	-0.28 (P)
6. Sativol dimethyl ether	2.38	3.04	^d	2.08	2.98	2.84
7. Sativol diacetate	2.15	2.97	^d	1.94	2.82	2.50
6 minus 7	-0.23 (P)	-0.07 (M)		-0.14 (M)	-0.16 (O)	-0.34 (O)
8. Lucernol trimethyl ether	2.66	^d	3.01	2.08	2.96	2.82
9. Lucernol triacetate	2.18	^d	2.60	1.94	2.80	2.51
8 minus 9	-0.48 (O, M)		-0.41 (O, M)	-0.14 (M)	-0.16 (O)	-0.31 (O)
10. 7,11,12-Trimethoxycoumestan	2.15	3.05	3.03	2.48	^d	2.82
11. 7,11,12-Triacetylcoumestan	2.02	2.82	2.69	2.11	^d	2.41
10 minus 11	-0.13 (M)	-0.23 (O)	-0.34 (O)	-0.37 (O, M)		-0.41 (O, M)

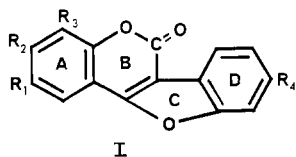
^a Measured from TMS at 60 mcs. in units. All spectra run in 1,1,2,2-tetrachloroethane at 120° C. Negative value indicates resonance at lower field in acetate.

^b Unassigned at present because of spectra complexity.

^c Location of substituting hydroxyl.

^d Substituted position.

those of coumestrol (I, $R_1 = R_3 = H$, $R_2 = R_4 = OH$) first suggested that



these compounds were coumestans closely related to coumestrol (Tables I and II).

Lucernol. The formation of a triacetate and a trimethyl ether confirmed the presence of three free hydroxyl groups in lucernol. Alkaline fusion of lucernol gave two compounds that were identified as resorcinol and hydroxyhydroquinone, giving an indication of the number and possible position of the hydroxyl groups on the two rings (Table III).

The 60-mcs. PMR spectrum of lucernol acetate shows the presence of a low-field ortho doublet, $\tau = 1.94$ (splitting = 8.5 c.p.s.) and a singlet at $\tau = 2.18$ (from TMS as internal standard). These low field resonance bands are characteristic of 5- and 10- protons in coumestans (12, 13). Since neither the 5- or 10-positions may be substituted, only two possible structures can be assigned to lucernol—7,11,12-trihydroxycoumestan or 6,7,12-trihydroxycoumestan.

The λ_{max} of the ultraviolet spectrum of lucernol in alcohol underwent a bathochromic shift of 20 $m\mu$ in the presence of sodium acetate which indicated a hydroxyl group at the 7-position (17) (Table I). The combination of boric acid and sodium acetate produced a shift of 7 $m\mu$, as would be expected for an orthodihydroxyl grouping (10). Thus, the ultraviolet spectrum is compatible with the two possible structures suggested by PMR but does not permit a choice between them. Comparison of the physical properties of lucernol with 7,11,12-trihydroxycoumestan (3) proved them to be different. Thus, the structure of lucernol must be 6,7,12-trihydroxycoumestan. On the basis of this structure, the remaining protons can be assigned as in Table II.

Sativol. Analysis of sativol, its acetate, and its methyl ether indicated that it was a monomethoxy compound containing two hydroxyl groups. Alkaline fusion of sativol gave a mixture of four compounds that were identified as resorcinol, β -resorcylic acid, pyrogallol, and pyrogallol carboxylic acid. As with lucernol, these products suggested the presence of one oxygen-containing functional group on one ring and two on the other. Their possible positions are indicated in Table III.

Controlled systematic degradation was employed to locate the functional groups on sativol. Methylative ring opening employing alkaline methyl sulfate formed

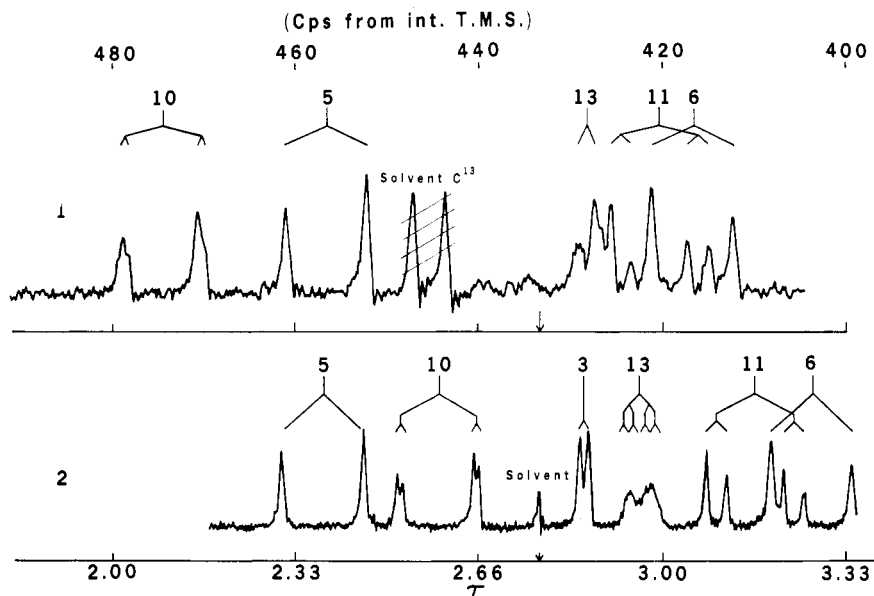
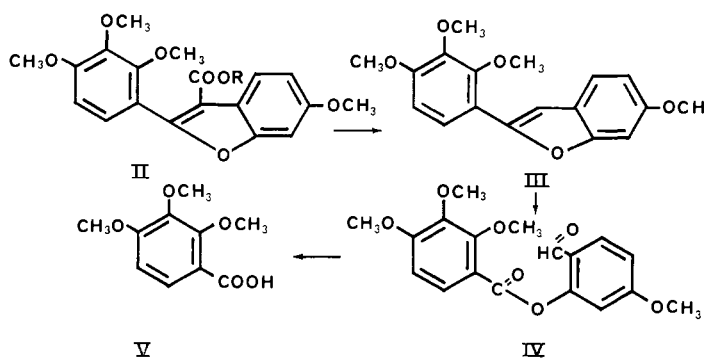


Figure 1. Proton magnetic resonance

1. Sativol dimethyl ether in 1,1,2,2-tetrachloroethane
2. 2-(2',3',4'-Trimethoxyphenyl)-6-methoxybenzofuran (III) in deuteriochloroform

a tetramethyl ether-methyl ester (II, $R = CH_3$). Hydrolysis to the carboxylic acid (II, $R = H$) followed by decarboxylation gave the benzofuran (III). The benzofuran was then ozonized and the product reduced to a crystalline aldehyde (IV). Hydrolysis of this aldehyde gave an acid (V) which must have been derived from ring A. The identification of the acid as 2,3,4-trimethoxybenzoic acid located the functional groups at the 7- and 8-positions.



The 60-mcs. PMR spectra of the methyl ether in 1,1,2,2-tetrachloroethane (TCE) and the benzofuran (III) in deuteriochloroform established the position of the hydroxyl group in the D ring. The spectra of the benzofurans of the three related coumestans—coumestrol, trifoliol, and medicagol—assisted in the proton assignments (Figure 1). Decarboxylation of sativol methyl ether did not change the position of the $\tau = 2.38$ ortho doublet (splitting = 9.0 c.p.s.) (Figure 1), whereas it shifted the $\tau = 2.08$ para-split ortho doublet (splitting = 8.5, 0.7 c.p.s.) upfield to $\tau = 2.59$. As was shown previously (72), these bands

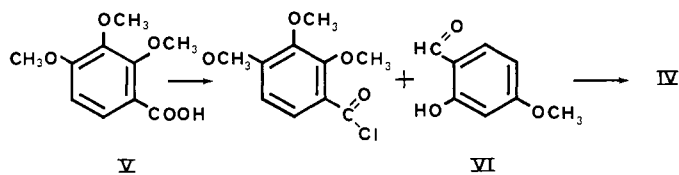
Table III. Possible Ring Substitution Sites from Fusion Products

Compounds	Rings	
	A	D
Lucernol		
a. Resorcinol	5 or 7	10 or 12
b. Hydroxyhydroquinone	(6 and 7) or (5 and 6)	(11 and 12) or (10 and 11)
Sativol		
a. Resorcinol	5 or 7	10 or 12
b. Pyrogallol	7 and 8	12 and 13

can be assigned only to the 5- and 10-proton. Since decarboxylation has an appreciable effect only at the 10-position, the ortho doublet must be assigned to the 5-proton and the ortho-para doublet to the 10-proton. Further evidence for the presence of a 13-proton was provided by the 1-c.p.s. splitting of furanyl resonance at $\tau = 2.89$, for it is known that only a proton at the 13-position has a detectable long-range coupling to this proton in a benzofuran (73). An ether linkage at the 8-position was strongly indicated by the shielding of the 5-proton which was approximately 0.3 p.p.m. greater than in any of the

previously reported coumestans (12, 13) where this position is unsubstituted. Diehl (6) reported a para substituent effect of 0.33 p.p.m. for the methoxyl group in meta- and para-disubstituted benzenes. Thus, the D ring is substituted at the 12-position, and the substitution of the A ring at the 7- and 8-positions is confirmed. The remaining peaks of the aromatic region can be immediately assigned as shown in Figure 1.

The intermediate aldehyde (IV) must therefore be 4-methoxy-2-(2',3',4'-trimethoxybenzoyl)benzaldehyde. This structure was confirmed unequivocally by its synthesis from 2,3,4-trimethoxybenzoic acid and 2-hydroxy-4-methoxybenzaldehyde.



The λ_{max} of sativol in alcohol (Table I) did not undergo a bathochromic shift in the presence of sodium acetate or boric acid-sodium acetate, as would be expected if sativol contained a hydroxyl group at the 7-position (11) or an ortho-dihydroxyl grouping (10). Since sativol did not undergo these shifts, the lone methoxyl group must be at the 7-position, and the hydroxyl group must therefore be at the 8-position.

The location of the lone methoxyl group at the 7-position was confirmed by PMR spectroscopy through a comparison of the ether-acetate shift of the aromatic protons of sativol with those observed for several coumestans of known structure. Smith (14) suggested an ortho shielding constant (referred to unsubstituted benzene) of 0.21 p.p.m. for the acetate and 0.45 p.p.m. for the methoxyl group from a study of disub-

stituted benzenes. Thus, substitution of an acetate for a methoxyl group, while both structure and solvent are otherwise constant, should cause a downfield shift of roughly 0.24 p.p.m. Table II shows the shielding of ring protons in acetate and methoxy derivatives of sativol and a series of model compounds. The peak from the 6-proton in sativol shows a small shift which corresponds to the meta shifts of the 5- and 10-protons of coumestrol, its 4'-O-methyl ether, 7,11,12-trihydroxycoumestan, and the 5-proton of trifoliol. This shift shows that the hydroxyl group cannot be at the 7-position and therefore must be at the 8-position. Hence, the methoxyl must be at the 7-position. The shift of the 5-proton resonance as would be expected

for para-substitution further confirmed this assignment. The ortho shift of the 13-proton in sativol was entirely consistent with the corresponding shift in 4'-methoxycoumesterol and lucernol and in reasonable agreement with the value from Smith's data (14). Very low shifts for H-11 were obtained from sativol, coumestrol, and lucernol, although the corresponding value for trifoliol (where the hydroxyl group is in the 10- rather than the 12-position) appears to be normal. The spin-spin pattern for this proton in sativol is such that no confusion in its assignment is possible, and the shifts in the coumestrol series permit an unambiguous assignment.

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CHANGES DURING STORAGE

Effect of Cold Storage on Chlorogenic Acid Content of Potatoes

THE phenolic compounds of potatoes are involved in the enzymic browning of raw potatoes (12) and in the discoloration of cooked potatoes (8), and are also associated with injuries and diseases of potatoes (5, 10). Because of this, and their importance as metabolic components, phenolic compounds of potatoes have been studied widely.

Although the knowledge of phenolic

compounds of potatoes is increasing, there has been little investigation of the effect of storage on changes in the content of these compounds. Craft *et al.* (4) have shown that the total phenolic content in two varieties of potatoes, Russet Rural and Kennebec, does not change significantly during 5 months of storage at 40° and 55° F. or 3 months at 32° F. It increased, however, after 4 to

5 months of storage at 32° F. They suggested that the increase is not due to the storage temperature but is related to injury. The results obtained by Mondy *et al.* (13) are not in agreement with those of Craft *et al.* (4). The former reported that the total phenolic content of the cortex tissue of potatoes increased 25 to 75% from the time of harvest up to 3 months of storage at 40° F. The

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