Breads containing 25% mesquite fraction B (milled endocarp hulls) had reduced loaf volume and increased crumb firmness. The bread was much darker than the control and had a sandy texture due to the high fiber content. Fraction B may have some use as a dietary fiber, but its high BTU value (Table IV) probably gives it more value as a fuel. In the mesquite processing plant designed by Meyer (1984), it is incinerated to supply the hot air required to dry the pods before processing.

The seed gum is the most valuable component in fraction C. Its galactose to mannose ratio and viscosity (data not shown) are close to those of guar gum so it has applications and a commercial value similar to guar, i.e. as a food thickening agent or for use in oil-drilling operations. The seed coat in fraction C could be burned as a heat source.

Fraction D has the typical beaney, nutlike taste of other legumes and would be expected to have similar food and feed uses. The protein has a lower solubility than soy protein, good foam expansion, foam stability, and emulsifying properties (Meyer, 1984).

Registry No. C (14:0), 544-63-8; C (16:0), 57-10-3; C (18:0), 57-11-4; C (18:1), 112-80-1; C (18:2), 60-33-3; C (18:3), 463-40-1; lignin, 9005-53-2; cellulose, 9004-34-6; L-rhamnose, 3615-41-6; arabinose, 147-81-9; D-xylose, 58-86-6; D-mannose, 3458-28-4; D-glucose, 50-99-7; D-galactose, 59-23-4.

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Formation of Sodium Bisulfite Addition Products with Trichothecenones and Alkaline Hydrolysis of Deoxynivalenol and Its Sulfonate[1]

J. Christopher Young

The mycotoxin deoxynivalenol (DON) and its 3-acetyl derivative reacted quickly with aqueous sodium bisulfite at room temperature to form sulfonate salts. Addition of sodium bisulfite was shown to occur across the 9,10 double bond. The related compound nivalenol reacted about 4 times more quickly, while reactions with Ac_2DON and the DON isomer, isoDON, proceeded more slowly by about 7- and 60-fold, respectively; the triacetyl derivatives of DON and isoDON did not react at all. Although DON-S was stable under acid conditions, it was converted back to DON under alkaline conditions, especially at elevated temperature and pH. Subsequent rapid isomerization of DON to isoDON was observed at 75 °C in a variety of bases and solvents and resulted in the subsequent formation of another isomer of DON in addition to three lower molecular weight isomers.

INTRODUCTION

The presence of the mycotoxin 4-deoxynivalenol (DON, vomitoxin, 3α,7α,15-trihydroxy-12,13-epoxytrichothec-9-en-8-one) in grains (e.g., corn and wheat) contaminated by the fungus *Fusarium graminearum* Schwabe is of concern due to undesirable toxicological consequences when such material is used in human food or animal feeds. Recent studies have shown that levels of DON in contaminated grains can be reduced by at least 95% upon treatment with aqueous sodium bisulfite (Young, 1986; Young et al., 1986b). When bisulfite-treated contaminated soft white winter wheat was milled and baked, levels of DON increased to 50–75% of that in the corresponding wheat (Young et al., 1986b). Although those treatments examined were too drastic (on the rheological properties) for direct application to human foods (Young et al., 1986b), they were successful in detoxifying contaminated corn used

Plant Research Centre, Agriculture Canada, Ottawa, Ontario K1A 0C6.

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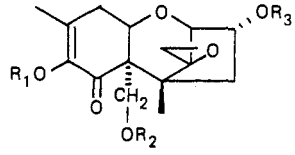
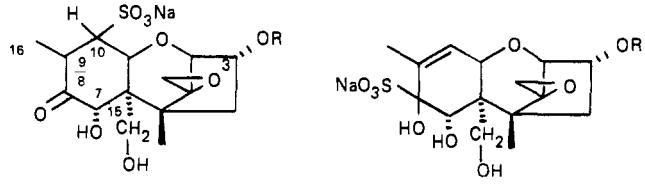
in pig feed (Young et al., 1986c). The present study was conducted to determine the structure of the bisulfite reaction product (DON-S) and the relative rates of reaction between sodium bisulfite and DON and several other trichothecenes. In addition, the stabilities of DON-S under acidic and basic conditions and DON in base were investigated.

MATERIALS AND METHODS

Materials. Nivalenol (NIV) (**1a**) was received as a gift from R. Black (U.K.). DON (**1b**) and 3-acetyldeoxynivalenol (AcDON) (**1c**), were prepared biosynthetically from liquid cultures of *Fusarium roseum* (ATCC 28114) (Greenhalgh et al., 1984b). 3,15-Diacetyldeoxynivalenol (Ac_2DON) (**1d**), 3,7,15-triacetyldeoxynivalenol (Ac_3DON) (**1e**), 3,8,15-triacetoxy-12,13-epoxytrichothec-8-en-7-one (triacetylisodeoxynivalenol, Ac_3isoDON) (**2b**), and isoDON (**2a**) were prepared according to Greenhalgh et al. (1984a).



2a R = H isoDeoxynivalenol (isoDON)
2b R = Ac 3,8,15 - Triacetylisodeoxynivalenol (Ac_3isoDON)

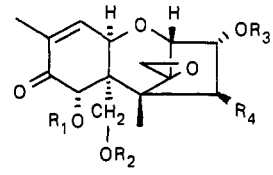


3a R = H Deoxynivalenol sulfonate (DON-S) 5a
3b R = Ac 3 - Acetyldeoxynivalenol sulfonate (AcDON-S) 5b

Analyses. Aliquots from reaction mixtures were analyzed by high-performance liquid chromatography (HPLC) using a Waters Scientific Radial-PAK cartridge packed with C18 Novapak (5 μm) coupled to a Perkin-Elmer LC-85 variable-wavelength ultraviolet (UV) detector. The column was eluted with methanol–water (1:1) at 2 mL/min. Quantitation of HPLC analyses was achieved by using a Varian Vista 402 chromatography data system.

Spectral Determinations. Infrared (IR) spectra were determined as KBr pellets on a Beckman IR-20A spectrometer. Ultraviolet spectra were determined in methanol on a Unicam SP1800 spectrophotometer. Electron impact (EI) and fast atom bombardment (FAB) mass spectrometry (MS) were carried out on a Finnigan MAT 312 mass spectrometer. Gas chromatographic (GC)–MS determinations were made using a DB-5 bonded phase fused silica capillary column (20 m × 0.32 mm i.d.) temperature programmed from 100 to 260 °C at 10 °C/min. ^{1}H and ^{13}C nuclear magnetic resonance (NMR) spectra were run in Me_2SO-d_6 on a Bruker WM-250 spectrometer under the conditions described by Blackwell et al. (1984); confirmation of ^{1}H chemical shift assignments was made by ^{1}H homonuclear correlation (COSY), and ^{13}C chemical shift assignments were made by the DEPT pulse sequence to determine the number of directly attached protons corresponding to each resonance.

Reaction of Trichothecenones with Sodium Bisulfite. Various trichothecenones [NIV (**1a**) (52 μg), DON (**1b**) (50 μg), AcDON (**1c**) (58 μg), Ac_2DON (**1d**) (65 μg), Ac_3DON (**1e**) (72 μg), isoDON (**2a**) (50 μg), Ac_3isoDON (**2b**) (72 μg)] were each treated at room temperature with 1.0 mL of aqueous sodium bisulfite containing the equivalent of 10% SO_2 (w/w). Aliquots of each reaction mixture were analyzed directly by HPLC at the appropriate wavelength: NIV, 220 nm; DON, 220 nm, AcDON, 220 nm; Ac_2DON 220 nm; Ac_3DON, 220 nm; isoDON, 280 nm; Ac_3isoDON, 250 nm.



	R_1	R_2	R_3	R_4	
1a	H	H	H	OH	Nivalenol (NIV)
1b	H	H	H	H	Deoxynivalenol (DON)
1c	H	H	Ac	H	3-Acetyldeoxynivalenol (AcDON)
1d	H	Ac	Ac	H	3,15 - Diacetyldeoxynivalenol (Ac_2DON)
1e	Ac	Ac	Ac	H	3,7,15 - Triacetyldeoxynivalenol (Ac_3DON)

Preparation of the Sulfonates of DON (DON-S) (3a) and AcDON (AcDON-S) (3b). To 5 mg of DON was added a solution of 400 mg of sodium bisulfite in 2 mL of water. After standing overnight at room temperature, the reaction mixture was placed onto a C_{18} SEP-PAK, washed with water (2 mL), and eluted with methanol (6 mL). The eluate was taken to dryness and made to 1 mL in methanol. Aliquots of this solution containing DON-S were taken for the hydrolysis reactions.

For spectral characterization of AcDON-S, 15 mg of AcDON was similarly treated with a solution of 1200 mg of sodium bisulfite in 6 mL of water and worked up to give 22 mg of a white solid. This residue was purified by preparative thin-layer chromatography on Whatman LKD6F silica gel (ethyl acetate–methanol 9:1) and gave AcDON-S as a white solid: 6.4 mg; R_f 0.15; IR 3430, 1725 cm^{-1}; UV, end absorption; FAB-MS m/z 443; ^{1}H NMR δ 1.04 (3 H, H-14), 1.28 (3 H, H-16, $J_{16,9}$ = 6.8 Hz), 2.0, 3.1 (2 H, H-4, m), 2.08 (3 H, Ac CH_3), 3.00, 3.15 (2 H, H-13, J_{AB} = 3.9 Hz), 3.24 (1 H, H-9, $J_{9,16}$ = 6.8 Hz, $J_{9,10}$ = 1.5 Hz), 3.68 (1 H, H-10, $J_{10,11}$ = 2.2, $J_{10,9}$ = 1.5 Hz), 3.83 (1 H, H-2, $J_{2,3}$ = 4.3 Hz), 3.83, 4.10 (2 H, H-15, J_{AB} = 4.3 Hz), 4.66 (1 H, H-7), 4.99 (1 H, H-3, $J_{3,2}$ = 4.3 Hz), 5.13 (1 H, H-11, $J_{11,10}$ = 2.1 Hz); ^{13}C NMR δ 11.4 (C-16), 13.8 (C-14), 20.8 [CH_3(Ac)], 39.6 (C-9), 41.2 (C-4), 46.6 (C-5), 48.5 (C-13), 55.0 (C-6), 60.4 (C-15), 66.3 (C-12), 68.8 (C-11), 72.5 (C-3) (tentative assignment), 73.3 (C-7) (tentative assignment), 77.3 (C-10) (tentative assignment), 79.8 (C-2), 172.5 [C=O(Ac)], 211.7 (C-8).

Hydrolysis of DON-S. Typically, 140 μg of DON-S was treated with 200 μL of an aqueous solution of various acids or alkalies at either room temperature or 75 °C. Aliquots were periodically removed and analyzed directly by HPLC (at 220 nm) for appearance of DON.

Alkaline Hydrolysis. (a) DON. Mixtures of DON (250 μg) in 0.1 M NaOH, Na_2CO_3, or tetrabutylammonium hydroxide in water, NaOH or NaOMe in methanol, or NaOEt in ethanol (500 μL each) were heated in sealed vials at 75 °C. Aliquots were periodically removed and analyzed directly by HPLC for DON and its rearrangement products.

(b) Ac_3DON. A mixture of A_3DON (200 μg) in 0.1 M aqueous NaOH (400 μL) was heated at 75 °C. Aliquots were periodically removed and analyzed directly by HPLC for Ac_3DON, DON, isoDON, and the rearrangement products.

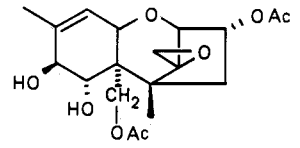
(c) DON-S. A mixture of DON-S (100 μg) in 0.1 M aqueous NaOH (200 μL) was heated at 75 °C. Aliquots were periodically removed and analyzed directly for DON

and its rearrangement products.

(d) isoDON and Ac_3isoDON. Mixtures of isoDON (160 μg) or Ac_3isoDON (115 μg) in 0.1 M aqueous NaOH (200 μL) were heated at 75 °C. Aliquots (10 μL) were periodically removed and neutralized in ice-cold 0.1 M HCl (10 μL) and the resultant mixture analyzed by HPLC for isoDON, Ac_3isoDON, DON, and the rearrangement products.

RESULTS AND DISCUSSION

Reaction of Tricothecenones with Sodium Bisulfite. The rate of reaction between trichothecenones and sodium bisulfite was greatly influenced by the location of the α,β-unsaturated enone system and the nature of nearby substituents. DON (**1b**) and its 3-acetyl derivative AcDON (**1c**), each with a 9-en-8-one system, reacted quite quickly under the conditions employed, with half-lives of 20 min each for starting material. Nivalenol (**1a**), with the same chromophore, reacted more quickly (half-life 5 min). The 3,15-diacetyl derivative **1d** reacted more slowly (half-life 150 min), and when the 7-hydroxyl adjacent to the ketone was also acetylated as in Ac_3DON (**1e**), there was no reaction. By contrast, isoDON (**2a**) with an 8-enol 7-one system reacted exceedingly slowly (half-life 1200 min), presumably because of steric hindrance by the methyl group at the position β to the ketone, and Ac_3isoDON (**2b**) failed to react at all. The non-keto trichothecene dihydrocalonectrin (**4**) (present as an impurity in one sample of AcDON) also did not react with bisulfite.



4 Dihydroxycalonectrin

Bisulfite normally reacts with α,β-enones at either the keto or β-positions (Royals, 1954). Thus, for DON and AcDON, two possible products from reaction with sodium bisulfite would be the 10-sulfonates **3a** and **3b** or the 8-hydroxy sulfonates **5a** and **5b**, respectively. Loss of UV absorption typical for the α,β-enone chromophore confirms that reaction occurred within this system. FAB-MS fragments at m/z 401 and 443, respectively (for $M + H^+$), are consistent with only 1 equiv of sodium bisulfite having been added. The IR spectra indicate that the carbonyl was not affected. The ^1H NMR spectrum of AcDON-S showed chemical shifts and splitting patterns similar to those of AcDON and other related trichothecenes (cf. Blackwell et al., 1984) in the B, C and epoxide ring portions of the molecule. However, several diagnostic features of the ^1H NMR spectrum are worth noting. The appearance of the C-16 methyl group as a doublet (J = 6.8 Hz) at 1.3 ppm (shifted upfield from 1.8 ppm in AcDON) suggests addition of a proton at that previously unsaturated position. Concomitant loss of unsaturation at C-10 was indicated by a marked upfield shift (to 3.7 from 6.6 ppm) of the C-10 resonance. In the ^{13}C NMR spectrum, most resonances were similar to those in the starting material. However, two exhibited significant upfield shifts. Appearance of the C-9 and C-10 resonances at 39.6 and 77.3 ppm (from 135.8 and 138.4 ppm, respectively) is also suggestive of loss of unsaturation at this position. Taken together, all the spectral data support the 10-sulfonate structure **3b** for the sulfonate product. In addition, the 2D ^1H NMR correlation spectrum showed couplings between the C-16, -9, -10, and -11 protons consistent with that expected for structure **3b**, and the ^{13}C spin–echo multiplicity sorting spectrum showed that the resonances assigned to C-9, -10, and -11 were all due to methine carbons.

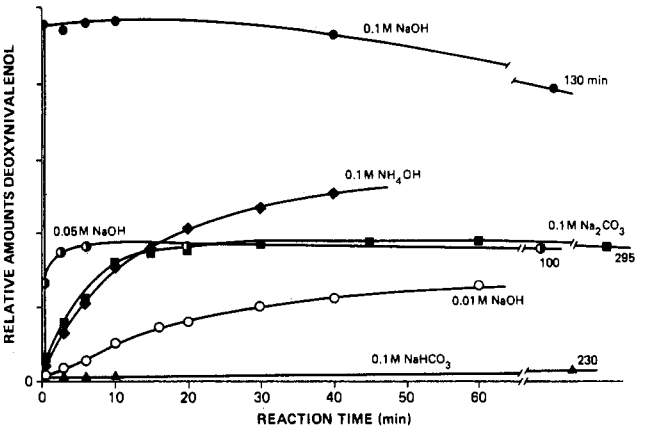


Figure 1. Formation of deoxynivalenol by treatment of deoxynivalenol sulfonate with various aqueous alkalies at room temperature.

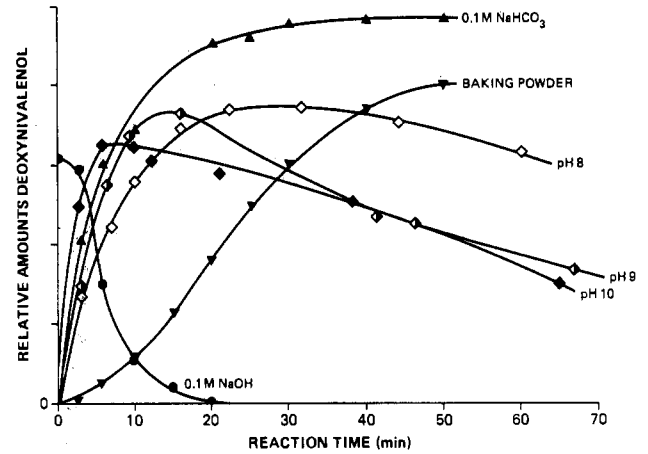


Figure 2. Formation of deoxynivalenol by treatment of deoxynivalenol sulfonate with various alkalies at 75 °C.

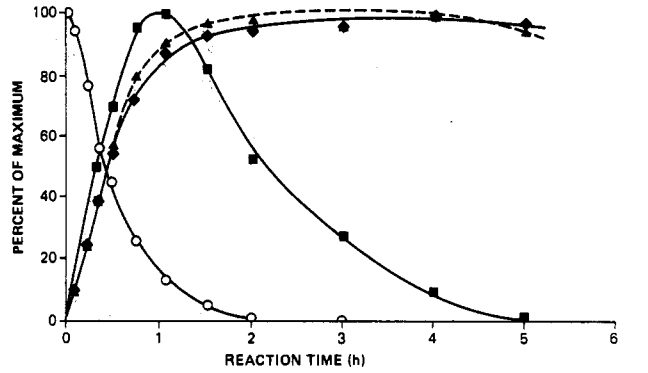


Figure 3. Formation of rearrangement products by treatment of deoxynivalenol (DON) with 0.1 M methanolic NaOH at 75 °C: (○) DON; (■) norDON-A; (♦) norDON-B; (▲) norDON-C.

Hydrolysis of DON-S. DON-S was stable in acid solution but underwent hydrolysis back to the parent DON under basic conditions. The rate of hydrolysis was dependent upon the pH and temperature (Figures 1 and 2) and was a maximum at the upper limits employed. At room temperature, hydrolysis ranged from instantaneous in 0.1 M NaOH to practically nil in 0.1 M $NaHCO_3$. However at 75 °C, DON-S was converted quite quickly to DON by $NaHCO_3$ and baking powder. Young et al. (1986b) showed that the presence of $NaHCO_3$ in the dough was partially responsible for the reappearance of DON in

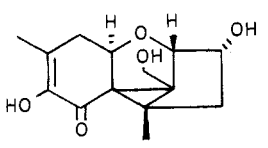
Table I. Reactions of Various 0.1 M Bases With Deoxynivalenol (DON) and Related Compounds at 75 °C

compd	base	solvent	$T_{1/2}$, min		time for max appearance, min		
			DON	norDON-A	norDON-A	norDON-B	norDON-C
DON	NaOH	H_2O	6	50	35	60	100
	NaOH	MeOH	26	70	65	190	190
	Na_2CO_3	H_2O	35	50	90	195	150
	NaOMe	MeOH	37	70	60	130	130
	NaOEt	EtOH	12	55	30	90	90
	Bu_4NOH	H_2O	7	55	20	150	100
Ac_3DON	NaOH	H_2O	9	50	25	55	55
isoDON	NaOH	H_2O	1.0[a]		6	10	10
Ac_3isoDON	NaOH	H_2O	0.7[a]		8	8	9

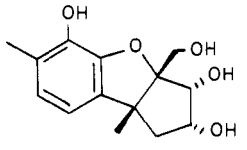
[a] For isoDON.

cookies baked from contaminated wheat that had been treated with sodium bisulfite. At 75 °C in base, the presence of DON was transitory, especially at the highest pHs (Figure 2).

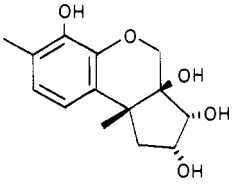
Alkaline Hydrolysis of Trichothecenones. When treated with 0.1 M methanolic NaOH at 75 °C, DON rapidly disappeared and three new products, designated norDON-A (**6**), norDON-B (**7**), and norDON-C(**8**), were observed (Figure 3). The characterization of these com-



6 norDON-A



7 norDON-B



8 norDON-C

pounds has just been reported (Young et al., 1986a). The loss of DON was complete after about 2 h and nearly coincided with the maximum appearance of the three products. These compounds were unstable under these conditions, and they too began to disappear, norDON-A much more rapidly than the others. The rearrangement is not specific base or solvent dependent (see Table I) since similar patterns were observed when other bases and/or solvents were employed. The main influence of base and solvent was on the rate and reflected the influence of pH noted for hydrolysis of DON-S to DON and subsequent decomposition. No other products or intermediates were detected by HPLC.

The alkaline hydrolysis of Ac_3DON to DON occurred instantaneously, since starting material was not detected even after only 30 s and a pattern virtually identical with that of Figure 3 was observed. By contrast with the alkaline hydrolysis of DON, degradation of isoDON to the same three products proceeded more quickly by almost 1 order of magnitude (Table I), and DON was not observed. In the presence of base, Ac_3isoDON disappeared within 1 min and the corresponding transient appearance of isoDON was followed by rapid formation of norDON-A, norDON-B, and norDON-C (Figure 4; Table I).

These kinetic data suggest that the sulfonates and acetyl derivatives of DON in base are hydrolyzed rapidly to DON (**1b**), which is then slowly converted to isoDON (**2a**); in turn, isoDON is quickly degraded to norDON-A (**6**), norDON-B (**7**), and norDON-C (**8**). The triacetyl derivative (**2b**) of isoDON is hydrolyzed directly to isoDON. A

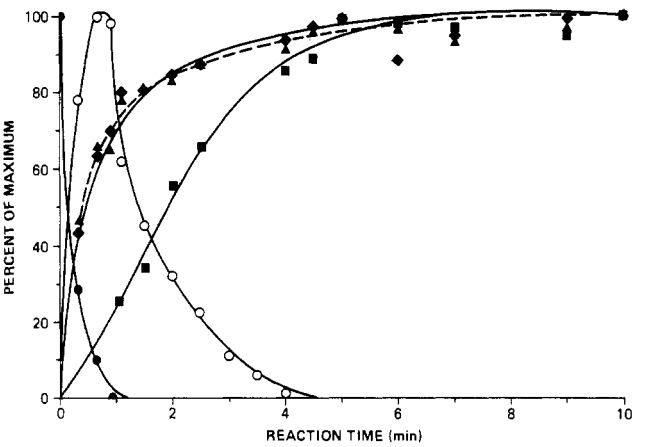


Figure 4. Formation of rearrangement products by treatment of 3,8,15-triacetylisodeoxynivalenol (Ac_3isoDON) with 0.1 M aqueous NaOH at 75 °C: (●) Ac_3isoDON; (○) isoDON; (■) norDON-A; (♦) norDON-B; (▲) norDON-C.

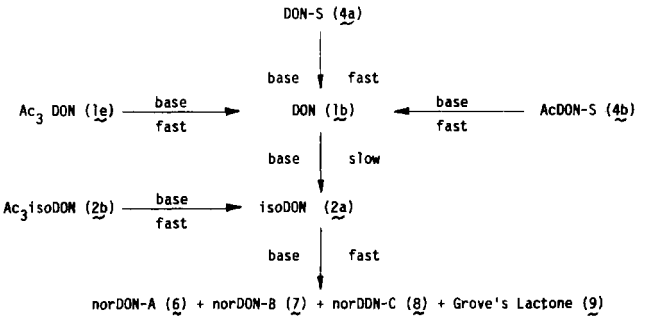
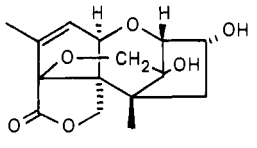


Figure 5. Proposed reaction scheme for alkaline hydrolysis and degradation of trichothecenones.

scheme summarizing the data is shown in Figure 5.

Grove (1985) described the alkaline rearrangement of DON to the isomeric epoxy lactone **9**. Since this com-



9

pound reportedly does not absorb in the UV, it was not observed by HPLC. However, reexamination of GC–MS data for rearrangement reaction mixtures revealed the presence of minor components having ions at m/z 296 for the free alcohol, 338 for the acetate, and 392 for the trifluoroacetyl derivative; all three compounds showed a major fragment ion at m/z 278. Since Grove (1985) did not report the full mass spectrum of his acetate derivative of **9** (only a strong M − 60 ion at 278), one can only speculate that it is indeed the same as that observed in

this study.

The alkaline hydrolysis of DON may be a general reaction for trichothecenes having identical functionalities in the A ring. Under the same conditions, the related trichothecene nivalenol (**1a**) produced three products having HPLC and UV properties similar to those of norDON-A, norDON-B, and norDON-C. Insufficient quantities of material prevented further characterization of these products. Grove (1985) also noted the formation of a related lactone from nivalenol.

Summary. Other related studies (Young et al., 1986b,c) have demonstrated that bisulfite treatment shows promise for the detoxification of DON contaminated grains and that the resultant product, DON-S, appears to be nontoxic to pigs (Young et al., 1986c). In addition to DON, *Fusarium spp.* are capable of producing quite a wide variety of other trichothecenes and mycotoxins (Blackwell et al., 1985; Greenhalgh et al., 1986a,b). Some of these metabolites may be partly responsible for the observed variability in toxicity of DON-contaminated pig feeds (Foster et al., 1986). Knowledge of the scope of potential detoxification methods is of considerable practical value. In this study, trichothecenes having a conjugated 9-en-8-one group were shown to undergo facile reaction with sodium bisulfite to form sodium sulfonate salts that are stable in acid but are rapidly hydrolyzed back to the parent compound in base. In addition, these keto trichothecenes undergo rearrangement and degradation to novel compounds in the presence of alkali.

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Registry No. **1a**, 23282-20-4; **1b**, 51481-10-8; **1c**, 50722-38-8; **1d**, 56676-60-9; **1e**, 51550-28-8; **2a**, 103776-41-6; **2b**, 92397-71-2; **3a**, 103776-36-9; **3b**, 103776-37-0; norDON-A, 103776-38-1; norDON-B, 103776-39-2; norDON-C, 103776-40-5.

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Flavor Chemistry of Cashew Apple Juice

Maria I. Maciel,[1] Thomsen J. Hansen,* Scott B. Aldinger, and John N. Labows[2]

The volatile constituents of commercially processed and unprocessed cashew apple juice were analyzed by headspace concentration gas chromatography–mass spectrometry. Specific analyses of sulfur-containing compounds were also performed. The major components were esters. However, alcohols, aldehydes, ketones, acids, terpenes, and sulfur-containing compounds were also identified. Except for sulfur dioxide, which had been added as a preservative to the processed juice, there were only minor differences between the two juices. Odor assessment suggested that certain esters and two aliphatic acids are important to the characteristic sickly sweet and sharp flavor of cashew apple juice. However, the overall aroma is the result of the integrated contributions of many components. Sensory evaluation revealed that the two juices were noticeably different from each other. However, they did not differ significantly in sweetness, sourness, bitterness, or fruitiness, and there was no preference for either type of juice. Slight changes in volatiles composition may be responsible for subtle changes in this complex flavor.

INTRODUCTION

The cashew tree (*Anacardium occidentale* L.), which originated in Brazil, is now grown in many tropical and subtropical countries. The cashew nut is its most important product with a world production of about 5×10^5 tons/yr (Tyman, 1980; FAO, 1983). The tree also yields an important product, the cashew "apple", to which the cashew nut is attached. Botanically, cashew apple is not a true fruit, but it has a pear shape, weighs about 10–15 g (approximately 3–6 times more than the nut, the "true fruit"), and is from 6 to 10 cm long. Its color varies from bright yellow to red, and it has a waxy skin. The cashew apple is very sour and astringent until fully ripe when it becomes edible. It is a very juicy fibrous fruit and can be consumed raw or in the form of jam, marmalade, juice, and distilled products.

Department of Nutrition and Food Sciences, Drexel University (M.I.M., T.J.H.), and Monell Chemical Senses Center (S.B.A., J.N.L.), Philadelphia, Pennsylvania 19104.

[1]Present address: Departmento de Nutrição, Universidade Federal de Pernambuco, 50.000 Cidade Universitária, Brazil.

[2]Present address: Colgate-Palmolive Co., Piscataway, NJ 08854.

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