crystallized the key intermediates four times from methanol to make absolutely certain no impurities were being carried along in the synthetic steps.

We must conclude that methyl- and/or dimethyl-thiophenes are not responsible for the fried character of onion flavor.

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Synthesis and Flavor Evaluation of Several Alkylfuranones Found in *Allium* Species (Onions, Shallots, and Leeks)

William G. Galetto* and Patrick G. Hoffman

Recently, the identification of two alkylfuranones (I and II) in the essential oils of several *Allium* species (onions, shallots, and leeks) has been reported. Their interesting structures and presence in significant quantitative amounts have prompted us to synthesize and organoleptically evaluate these compounds. We have found their flavor characteristics to be of a fatty-waxy nature, similar to aliphatic aldehydes and alcohols. They do not make a significant contribution to the flavor of the essential oil of onion.

In their study of the volatile components of onion oil Boelens et al. (1971) isolated and identified, by spectroscopic means, the novel alkylfuranone (II). More recently Dembele and Dubois (1973) reported the same compound as well as its higher homolog (I) in the essential oil of shallots. Schreyen et al. (1976) have identified both compounds in leek oil. These latter identifications in both cases were based primarily on mass spectral analysis.

Prior to our becoming aware of the work of Dembele and Dubois we had isolated and identified furanone (I) from the oil of onion (*Allium cepa*) and had assigned to it the name Cepanone. The other cyclic ketone (II) with the n-hexyl side chain we refer to as Norcepanone.
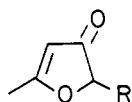
R = C_8H_{17}, Cepanone (I)

R = C_6H_{13}, Norcepanone (II)

The synthesis and the organoleptic evaluation of these two heterocyclic compounds are the subjects of this report.

EXPERIMENTAL SECTION

Materials. Crude undecyl-1,3-diyn-5-ol and tridecyl-1,3-diyn-5-ol were custom synthesized by Farchan

Chemical Company using the general procedure of Cook et al. (1952). Their initial attempts to purify the C_{11} alcohol by vacuum distillation resulted in detonation (Chanan, 1972). The reason is unknown; similar compounds have been routinely purified by distillation, see, e.g., Cook et al. (1952). Armitage et al. (1952), however, had a similar experience with iodoocta-1,3-diyne. We utilized the crude, undistilled alcohols which contained a small amount of the starting aldehyde reactant as the only significant impurity.

Norcepanone (II). This compound was prepared using the general method reported by Nazarova et al. (1967) for the cyclization of diacetylene alcohols using mercuric salts. Approximately 40 g of crude undecyl-1,3-diyn-5-ol, 40 ml of water, 100 ml of ethanol, and 4 g of $HgSO_4$ were combined and stirred at room temperature for 20 h forming a heavy precipitate and a yellow supernate. The reaction mixtures from two such reactions were combined and filtered, yielding a tarry solid and a yellow filtrate. The solid was stirred with several portions of ether; the ether was combined and concentrated. The resulting oil was steam distilled to give 15.6 g of crude furanone. The original filtrate upon vacuum concentration formed two phases. The organic phase, 16 g, contained about 44% of product by GLC analysis.
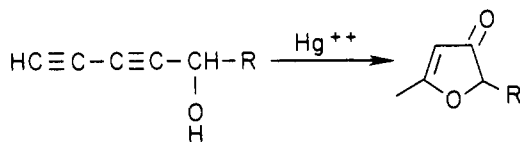
An aliquot of the combined crude product was purified by distillation: bp 78 °C (0.15 mm); n^{20}D 1.4682 [lit.
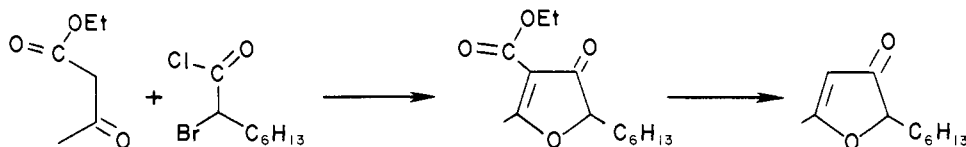
Scheme I

Scheme II

DeRijke and Boelens (1973): bp 79–81 °C (3 mm); n^{20}D 1.4715]. The MS, NMR, and ir spectra were essentially identical with those reported by Boelens et al. (1971).

Cepanone (I). This compound was prepared as described above except that tridecyl-1,3-diyn-5-ol was used as the diacetylene alcohol reactant. The crude product was fractionally distilled; an analytically pure center fraction was collected: 7.0 g; bp 127–129 °C (0.5 mm); n^{20}D 1.4680; mass spectrum (intensities in parentheses) 210 (3), 112 (6), 111 (61), 99 (9), 98 (100), 82 (7), 71 (7), 70 (10), 69 (10), 68 (10), 60 (8), 57 (21), 56 (14), 55 (13), 44 (7), 43 (14); ^{1}H NMR spectrum (60 MHz, CDCl$_3$) δ 0.87 (t, 3 H), 1.03–2.10 (m, 14 H), 2.23 (s, 3 H), 4.43 (t, 1 H), 5.42 (s, 1 H); ir spectrum (neat) 5.88, 6.26, 7.22, 7.42, 8.72, 10.6 μm.

Sensory Evaluation. Flavor thresholds of the pure compounds were determined in water by a trained group of eight panelists. Dilute samples were presented as a series in increasingly higher concentrations. The aroma descriptions were obtained using an odor blotter.

The effect of adding the furanones to an artificial onion oil was determined by tasting them at the 5% level. Equal weights (2.5%) of each of the standards were used; the resulting oils were evaluated in water at 0.1 ppm, by a triangle test method with 24 experienced panelists. The artificial onion oil was comprised of a mixture of alkyl di- and trisulfides (Galetto and Pace, 1973).

The same mixture of furanones in artificial onion oil was also added to hamburger, made into patties, and baked in an oven at 350 °F. Two descriptive panels were conducted, at 10- and 12-ppm onion oil levels to evaluate the patties.

To judge the role of the two furanones in natural onion oil a mixture of 3% cepanone (I) and 5% norcepanone (II) in natural Dutch onion oil was prepared. This mixture approximated the total furanone content of one of the Mexican onion oils. The mixture of furanones and natural onion oil was compared to the pure natural onion oil in two separate triangle tests with 20 experienced panelists participating in the first test and 18 panelists in the second test. For each test, the onion oils were diluted to 0.05 ppm in spring water.

RESULTS AND DISCUSSION

Norcepanone (II) has been prepared recently by DeRijke and Boelens (1973) in a two-step synthesis (Scheme I) in 7.6% overall yield. They suggested the low yield was due primarily to the fact that decarboxylation of the cyclic carboethoxy intermediate (Scheme I) could not take place until after ring opening had occurred.

We have used the procedure outlined by Nazarova et al. (1967) for the cyclization of conjugated acetylenic alcohols as shown in Scheme II. The starting materials are readily available from 1,4-dichlorobut-2-yne and the corresponding aldehydes (Cook et al., 1952) or as shown more recently by Fukumaru et al. (1975) by the coupling

Table I. Weight Percent of Furanones in Natural Onion Oils

Source	Cepa-none (I)	Norcepa-none (II)
Dutch	0.36	0.86
Mexican	3.3	5.8
Mexican	2.9	3.2
Egyptian	6.4	31.9

of 1-butyn-3-ol with the appropriate 1-bromoacetylenic compound. The cyclization goes smoothly at room temperature with the formation of elemental mercury.

Several samples of commercial onion oils from various geographical origins were analyzed in order to quantitate their content of the two furanones. The quantitative results, Table I, were obtained by comparing integrated GLC peak areas of single but representative analyses of the onion oils with the corresponding areas of a 5 and 50% solution of the appropriate furanone in ethyl alcohol. The furanone content is obviously very different in the various oils. The amount of norcepanone is consistently higher than that of its higher homolog. We have not examined enough authentic oils at this time in order to be able to determine if furanone content is a true indicator of geographical origin or authenticity.

Sensory Evaluation. When evaluated in dilute aqueous solutions by trained panelists, norcepanone (II) was found to have a threshold of 0.5–1.0 ppm; cepanone (I) was slightly less intense with a threshold of 1.0 ppm. Both can be best described as having fatty, waxy flavors similar to straight-chain aliphatic aldehydes or alcohols. Lesser, secondary flavor notes were of a meaty, burnt, musty nature. The aromas of both are similar in character to n-undecanal; however, they are much lower in overall intensity. The compounds linger on an odor blotter for at least 2 weeks.

The two furanones were evaluated together at the 5% level in an artificial onion oil by a triangle test method with 24 experienced panelists. Of the 12 correct responses, 9 commented on strength with $^2/_3$ of them finding the furanone-containing sample weaker in flavor.

The same mixture of furanones in artificial onion oil was also evaluated after being added to hamburger patties and baked at 350 °F. Two descriptive panels were conducted, at the 10- and 12-ppm oil levels. No flavor differences were found in either test between the artificial onion oil and the one containing the two furanones.

The flavor evaluations using natural Dutch onion oil involved the furanones at a higher level than in the case of the artificial onion oil. In these tests the total furanone content approximated that found in one of the Mexican oils, i.e. about 9% total (8% added and about 1.2% initial). In two separate triangle tests no significant differences were found in either test between the natural onion oil and the furanone enriched oil.

The furanones with their rather subtle, fatty flavors, when mixed with the very odorous polysulfides of onion oil, have no significant flavor impact on the final mixture. Our studies indicate that the furanones are not significant onion flavor components and, in fact, tend to dilute rather than enhance the flavor of both natural and artificial onion

flavors. We have not experimentally evaluated the furanones in either leek or shallot oil; however, due to their overall similarity to onion oil, we suspect the furanones play no significant flavor role in these products.

ACKNOWLEDGMENT

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Volatile Halogen Compounds in the Alga *Asparagopsis taxiformis* (Rhodophyta)

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The essential oil of *Asparagopsis taxiformis*, an edible red alga in Hawaii, is composed of mainly bromine- and iodine-containing haloforms with smaller amounts of other halogenated methanes and several halogenated ethanes, ethanols, formaldehydes, acetaldehydes, acetones, 2-propanols, 2-acetoxypropanes, propenes, epoxypropanes, acroleins, and butenones.

Limu kohu, which in Hawaiian means the supreme seaweed, is highly prized for its aroma and flavor (Abbott et al., 1974). Scientifically known as *Asparagopsis taxiformis* (Delile) Collins et Harvey, this red alga is a dioecious, gametophytic plant that alternates in its life cycle with a heteromorphic sporophyte known as *Falkenbergia rufanolosa* (Harvey) Schmitz. Curiously the male and female plants are odoriferous whereas the asexual plant is not. In a preliminary communication (Burreson et al., 1975) we reported that the major constituent in the essential oil of Hawaiian *A. taxiformis* is bromoform (1). More interestingly, we found that iodine-containing haloforms, the major one being dibromoiodomethane (2), are also present in the essential oil. Furthermore, several halogenated acetones and butenones were identified in the oil, suggesting strongly to us that the haloforms are formed in vivo by the well-known haloform reaction of methyl ketones. We have now carried out a more extensive examination of the volatile constituents of Hawaiian *A. taxiformis*, the subject of this paper, and have identified to date 42 components of the essential oil, 24 of these unreported by us in our earlier report (Table I).

ISOLATION

Male and female plants of *A. taxiformis*, which were not separated for this investigation, were obtained from the reefs on the Waikiki side of Diamond Head, Oahu between Sept, 1974 and June, 1975. The freshly collected, wet plants were processed for essential oil by drying the seaweed in a vacuum and trapping the volatile oil and water in a dry ice cooled condenser. The essential oil was separated from water by extraction with methylene chloride. Unfortunately, this latter procedure prevented us from determining whether substances such as chloroform and carbon tetrachloride were present in the oil. The essential oil, which was initially completely colorless, quickly developed a violet color on exposure to air and light due to the formation of iodine. Free molecular iodine, however, did not appear to be present in the live plants.

Separation of the essential oil was best achieved by chromatography on silica gel. Ten major fractions were collected and analyzed by Fourier transform proton magnetic resonance (^{1}H NMR) spectroscopy and gas chromatography–mass spectrometry (GC–MS). Fraction 1 contained three 1,1,3,3-tetrahalopropenes (30–32), a carbon tetrahalide (10), and a hexahaloacetone (25). Fractions 2 and 3 consisted of mostly haloforms (1–3, 5), but traces of other halogenated alkanes (7, 9, 13) were also present in fraction 2. Halogenated acetones (17, 20–22) and butenones (38–42), a 1,3,3-trihaloepoxypropane (29), and a trace of a carbonyl dihalide (11) were found in fractions 4–6. Fractions 7 and 8 were complex mixtures and none of the components have been characterized yet. Fraction 9 was mostly biogenetically unrelated benzaldehyde. Fraction 10 was also a complex mixture, but contained mostly a 2-haloethanol (12) and a small amount of a dihaloacetaldehyde (14). Compounds such as 30 and 38 were not formed during the chromatography as signals for these compounds were clearly visible in both the ^{1}H NMR and carbon-13 magnetic resonance (^{13}C NMR) spectra of the essential oil. Unfortunately, many of the iodinated compounds in the essential oil did not survive the adsorption chromatography. Iodoform (4), for example, could be readily seen in the ^{1}H NMR and mass spectra of the crude essential oil, but after chromatography on silica gel none of the fractions contained any iodoform. GC–MS analysis of fractions resulting from separation of the essential oil by molecular distillation or gel filtration

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