ammonium-3 propanoïque [2] dans l'osmorégulation. Mais, la structure et la polarité de ces composés conduiraient aussi à leur conférer un rôle dans l'ajustement de la perméabilité cellulaire en présence de chlorure de sodium. Nous nous proposons d'étudier ce rôle et de déterminer l'importance des composés à groupement sulfonium diméthylé dans les plantes adaptées aux biotopes littoraux.

PARTIE EXPERIMENTALE

Les spectres de RMN sont réalisés à 100 MHz.

Extraction. La fraction soluble totale est obtenue en EtOH (80%) à 0°.

Purification. Elle est réalisée par électrophoréchromatographie préparative sur papier Whatman 3 MM. L'électrophorèse en haute tension est effectuée à pH 2 (HCO_2H 0,75 N–40 V/cm–75 mn) et la chromatographie dans le solvant *n*-BuOH–HOAc–H_2O (12:3:5) pendant 15 hr. Après séchage des chromatogrammes, au four ventilé à 40°, les bandes contenant la bétaïne sont éluées avec HCl 0,001 N. L'éluat est concentré sous vide à 30°, puis repris dans l'eau. La bétaïne est ensuite précipitée à l'état de reineckate par addition d'une solution saturée acide de sel de reinecke. Le précipité est lavé 3 fois à l'eau distillée, puis repris dans Me_2CO 70%. La bétaïne est enfin libérée de son sel par une chromatographie de 14 hr dans le solvant *n*-BuOH–HOAc–H_2O, éluée, puis soumise à une dernière électrophorèse en haute tension à pH 2 (HCO_2H 0,75 N). La masse du produit recueilli, à l'état de chlorhydrate lyophilisé, est de 50 mg pour 10 g de matériel végétal sec.

Propriétés électrophorétiques. Les mobilités électrophorétiques (ME) du produit, exprimées par rapport à celles de la choline, sont déterminées à différents pH sur papier Whatman 3 MM; pH 2 (HCOOH 0,75 N), ME = 0,80; pH 3,4 (C_5H_5 N–HOAc–H_2O; 0,6:10:989,4), ME = 0,71; pH 3,9 (C_5H_5N–HOAc–H_2O; 7,5:25:967,5), Me = 0,20; pH 5,3 (C_5H_5N–HOAc–H_2O; 10:4:986), ME = 0,04; pH 8 ($CO_3(NH_4)_2$ 0,1 M), ME = 0,13; pH 11,3 (NH_4OH 0,2 N), ME = 0,11.

Propriétés chromatographiques. Le rapport R_c. distance parcourue par le composé/distance parcourue par la choline, est calculé, après développement des chromatogrammes dans différents solvants (20°, papier Whatman 3 MM); *n*-BuOH–HOAc–H_2O (12:3:5), R_c 0,85; BuOH–HCOOH–H_2O (15:3:2), R_c 0,64; *n*-BuOH–HCOOH–H_2O (3:1:1), R_c 0,71; *n*-BuOH–C_5H_5N–HOAc–H_2O (4:1:1:2), R_c 0,69; EtOH–NH_4OH–H_2O (15:4:1), R_c 0,76.

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2,3,4-TRITHIAPENTANE IN THE ESSENTIAL OIL FROM *HUMULUS LUPULUS*

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INTRODUCTION

The essential oil of hops is an extremely complicated mixture, containing well over 100 components [1]. Several of these are reported to contain sulphur, and recent investigations [2, 3] have led to the identification of *S*-methylthio-2-methylbutanoate, *S*-methylthio-4-methylpentanoate and 4,5-epithiocaryophyllene.

The composition of sulphur components in hops is modified by the traditional process of 'sulphuring' in which sulphur is burnt in the initial flow of hot air during the drying process [4]. This treatment with sulphur dioxide bleaches the hop bracteoles, improving the appearance of the hops on physical examination [5], and also considerably modifies the spectrum of sulphur compounds in the essential oil. We previously reported [6] the existence of a component which was prominent in the steam distilled oil from unsulphured hops but which was largely absent from oil obtained from sulphured hops. We now describe its identification as 2,3,4-trithiapentane. This is formed during the distillation process from a labile precursor which is destroyed when sulphuring is used.

RESULTS AND DISCUSSION

Initially, it was found that treatment of hop oil, from 'unsulphured' hops, with SO_2 had little effect on the level of the unidentified sulphur compound in the oil. This suggested that the sulphur compound was not present as such in the hops, but that it was present as an SO_2-sensitive precursor which was degraded during isolation (by steam distillation at 100°) of hop oil from the hops to form the sulphur compound. Confirmation was obtained when it was shown that the sulphur component was totally absent from hop oil isolated from the same batch of hops by a new process [7, 8], which involves steam distillation under low pressure at ambient temperature.

Chemical tests were carried out on a hop oil containing the unidentified sulphur compound, and the products and suitable controls were analysed by GLC using a flame photometric sulphur detector.,The sulphur compound was unaffected by treatment with aqueous solutions of hydroxylamine, sodium hydroxide and lead acetate, thus ruling out the possiblity of it being a thioester or a mercaptan. The sulphur compound was, however, completely removed by treatment with both aqueous mercuric chloride and hydrogen peroxide in glacial acetic acid. These results were consistent with the nature of the sulphur compound being a sulphide or polysulphide. Furthermore, the sulphur component was found to elute with the hydrocarbon fraction during column chromatographic separation of hop oil on Si gel, thus indicating the absence of polar groupings within the molecule.

A hop oil containing an enhanced level of the sulphur compound was prepared from a batch of 'unsulphured' hops. The hops were steam distilled at ambient temperature and a fraction containing 70% of the essential oil was collected. This fraction was discarded and the residual hops were then steam distilled at 100° to give a fraction enriched in the required sulphur compound. This sample was examined by C–GC–MS. A MS was obtained for the sulphur compound: m/e 128 $[M^+ + 2]$ (13%), 126 $[M^+]$ (100), 111 $[M^+ - Me]$ (16), 80 (17), 79 $[M^+ - SMe]$ (55), 78 (12), 64 $[S_2^+]$ (21), 47 (33), 46 (16) and 45 (48). This is in excellent agreement with that reported for 2,3,4-trithiapentane [9]. This structure was confirmed by peak enhancement studies, on polar and non-polar GLC stationary phases.

2,3,4-Trithiapentane has previously been established as a component of the essential oils of various species of onion, including *Allium tuberosum* (Chinese chive) [10], *Allium escalonium* (shallot) [11], *Allium sativum* (garlic) [12] and *Allium victorialis* (caucas) [13]. It is also claimed to be one of the major components contributing to the aroma of several boiled brassicaceous vegetables [14] including *Brassica oleracea* var. *gemmifera* (brussel sprouts), *Brassica oleracea* var. *capitata* (cabbage) and *Brassica oleracea* var. *botrytis* (cauliflower and broccoli). However, this is the first time that it has been reported as a component of hop oil. Typically, as shown by GLC, the level of 2,3,4-trithiapentane in oils from hops which have not been treated with sulphur dioxide is in the region of 100 ppm.

EXPERIMENTAL

Hop oils were isolated either by steam distillation at atmos. pres. according to the procedure recommended by the Institute of Brewing [15] or by the method of refs [7, 8]. Samples of hop oil were stored in glass ampoules sealed under vacuum. GLC employed synchronous flame ionisation and flame photometric detection. Stationary phases in use were 10% Carbowax 20M, and 3% OV-1, on chromosorb W; N_2 carrier gas flow rate 50 ml/min; temp. programme of 50° to 200° at 3°/min. Column chromatography was carried out using the method of ref. [16]. CGC–MS was performed on a Finnigan 3200 GC–MS system linked to a 6100 Data system (Masspec Analytical Speciality Services Ltd., Stroud, U.K.). The 30 m × 0.5 mm OV-1 glass SCOT column was linked directly to the source of the MS. A temp. programme of 60 to 260° at 4°/min was employed, and helium (1 kg/cm^2) was used as the carrier gas. The MS was operated with an isonisation voltage of 70 eV. The computer scanned continuously and collected data from m/e 40–560 every *ca* 1.6 sec.

Chemical tests were carried out on portions of a hop oil containing the sulphur component by treating them with respectively: (i) 7% aq. hydroxylamine, (ii) 5% aq. NaOH, (iii) 20% aq. lead acetate, (iv) satd (*ca* 6%) aq. $HgCl_2$ and (v) 30% aq. H_2O_2 in HOAc. Products were compared by GLC with products from the appropriate control experiments.

2,3,4-Trithiapentane was prepared by the reaction between methyl mercaptan (0.23 mol) and sulphur dichloride (0.10 mol) using the method of ref. [17]. After two distillations *in vacuo* (*ca* 0.10 mm Hg), the product (Found: C, 19.23; H, 4.97. Calc. for $C_2H_6S_3$: C, 19.03; H, 4.79%) exhibited the following physical properties. GC–MS 70 eV; m/e 128 $[M^+ + 2]$ (15%), 126 $[M^+]$ (100), 111 $[M^+ - Me]$ (14), 79 $[M^+ - SMe]$ (32) and 64 $[S_2^+]$ (10). PMR (90 MHz): δ 2.52 (6H, *s*). n_D 25 1.5983.

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