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BUTYLBORONATE ESTERS AS DERIVATIVES FOR GAS-CHROMATOGRAPHY-MASS SPECTROMETRY OF HOP CONSTITUENTS

S.J. Shaw

The Research Laboratory
Arthur Guinness Son & Co. (Dublin) Ltd.,
St. James's Gate, Dublin 8.

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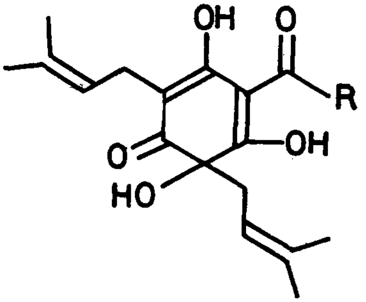
Hop resin acids of the humulone (I) and lupulone (III) types occur naturally as homologous series with differing acyl side-chains, and they undergo ready rearrangement, oxidation and cyclisation reactions to give complex mixtures of products(1). After conversion to their trimethylsilyl (TMSi) derivatives(2) useful gas chromatographic separations can be obtained, and the TMSi derivatives give good mass spectra on combined gas chromatography-mass spectrometry(3). However the TMSi derivatives of hop compounds have the disadvantage, frequently encountered with TMSi derivatives, that they rarely give molecular ions, and a search was made for an alternative type of derivative without this disadvantage.

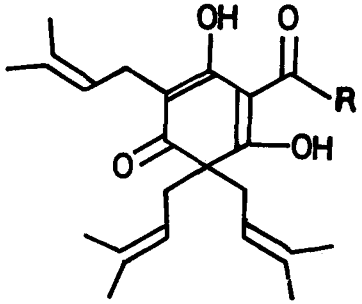
It has been found that hop resin acids readily form cyclic boronate esters with n-butylboronic acid. These derivatives behave well on gas chromatography-mass spectrometry, and in particular show molecular ions. Their fragmentation patterns differ from those shown by the TMSi derivatives, and the two types of derivative complement each other usefully in structural studies.

Gas chromatography-mass spectrometry of cyclic boronate esters was reported by Brooks and Watson(4) with 1,2- and 1,3-diols. With humulone (I), cohumulone (II), lupulone (III) and colupulone (IV) the reaction has been carried out by adding a slight excess of n-butylboronic acid to the hop constituent in either pyridine or dimethylformamide, and allowing the mixture to stand at room temperature for 30 mins. A suitable aliquot of the solution, injected onto a column of 1%F60 or 1% OV17, coated on silanised Gas Chrom P packed in a silanised glass column, gave discrete peaks for each of the compounds (I - V). Fig. I shows a typical chromatogram obtained from the boronate esters of humulone and colupulone. Tetracosane and octacosane have been included as standards.



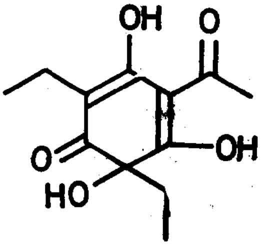
I.R = Bu^{i}

II.R = Pr^{i}

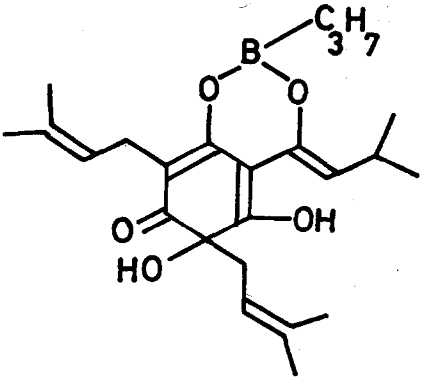


III. R = Bu^{i}

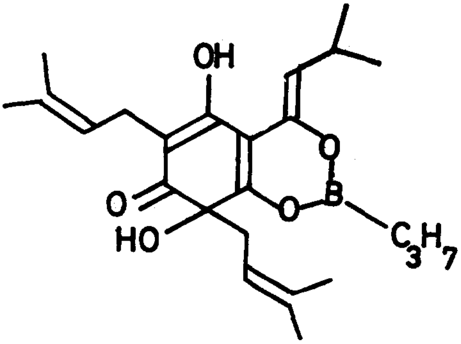
IV. R = Pr^{i}



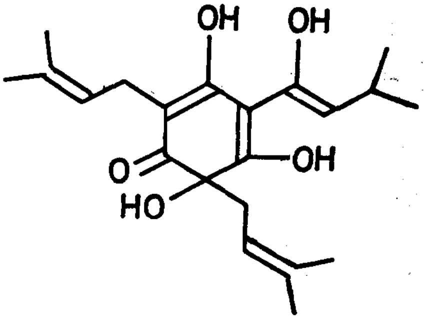
V



VI

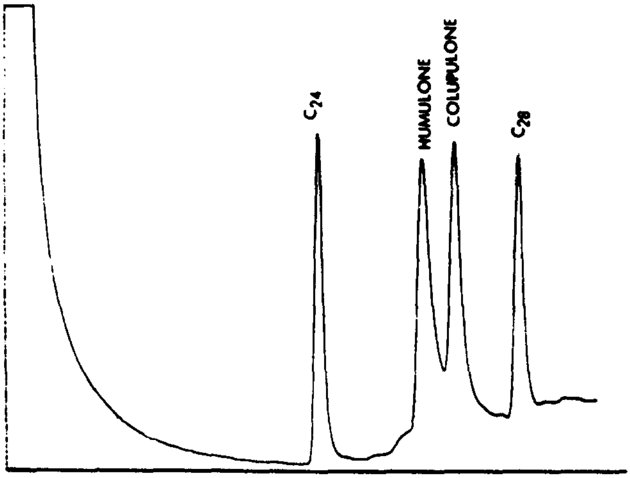


VII



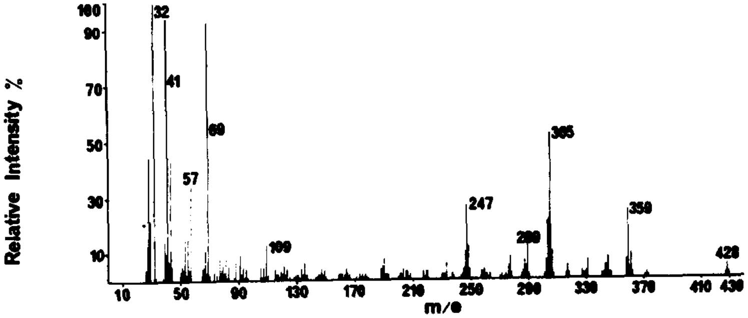
VIII

FIG. I



The mass spectra of the n-butylboronate esters of humulone (I), cohumulone (II), colupulone (IV) and of a humulone model compound (V), have been determined on an L.K.B. combined gas chromatograph - mass spectrometer. In each case a molecular ion was observed which corresponded to the addition of one molecule of n-butylboronic acid. Fig. II shows the mass spectrum of the boronate ester of humulone. The large peak at m/e 69 can be attributed to the isopentenyl ion, which also provides the base peak with the free resin acids(5).

FIG. II



The structures of the n-butylboronate esters may involve the acyl side-chains as in (VI) or (VII). It has been shown(3) that the TMSi derivatives of colupulone (IV) and humulone (I) probably involve enol-ether formation in the acyl side-chains. Acetyl acetone did not form an n-butylboronate ester. The formation of the boronate esters of the hop constituents is catalysed by basic solvents; these might be expected to favour a tautomeric form such as (VIII), which can readily form a cis planar 1,3-diol group.

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