99–100° (decomp.) but the small quantity of material available prevented complete characterization of this aldehyde.

Fraction VIII was a heavy, amber-coloured oil with an odour of pine needles and remained in a state of superfusion until seeded with *l*-bornyl acetate when it crystallized completely. After recrystallization from methanol and finally from ligroin, it had m.p. at 29°. Saponification with sodium hydroxide yielded 1-borneol, m.p. 208–208·5° in almost quantitative yield, and acetic acid was isolated from the sodium salt. This fraction consisted of *l*-bornyl acetate in a state of purity.

l-Bornyl acetate has previously been reported in two other New Zealand plants, *Agathis Australis*[6] and *Dacrydium Kirkii*.[7]

Fraction IX was a colourless, fragrant, mobile oil, the physical constants of which suggested either an oxygenated acyclic terpene compound or a monocyclic sesquiterpene. The low boiling point seemed to preclude the latter possibility, but analysis confirmed the formula, $C_{15}H_{24}$ (Found: C 88·30, H 12·2; calculated for $C_{15}H_{24}$: C 88·23, H 11·7%). Attempts to prepare crystalline hydrochloride, hydrobromide, nitrosochloride, nitrosite and nitrosate were unsuccessful.

Hydrogenation of this oil (5 g.) in alcohol (70 c.c.) using Adam's catalyst (0·1 g.) proceeded to completion within two hours. After twenty-four hours, hydrogenation was considered complete and the saturated product was distilled under reduced pressure. It had: b.p. 92°/2·4 mm., d_{20}^{20} 0·8621, n_D^{20} 1·4681. (Found: C 86·68, H 13·30. Calculated for $C_{15}H_{28}$, C 86·54, H 13·46%). Molecular refractivity: observed 67·0, calculated for $C_{15}H_{28}$ 67·10.

Dehydrogenation.—7 g. of this fraction mixed with 7 g. of sulphur in a pyrex tube were tested in a sodium nitrate bath at 200° c., the temperature gradually raised to 280° and maintained at that temperature for eight hours. Apart from a trace of azulene formed during the initial heating, neither azulene nor aromatic hydrocarbons could be isolated.

Ozonolysis.—The fraction (10 g.) dissolved in 150 c.c. of pure carbon tetrachloride was cooled in ice water and a gentle stream of ozonized oxygen bubbled through. After seventeen hours the colourless viscous ozonide was decomposed by gentle warming under reflux with water (10 c.c.). Isolation of the neutral and acid products in the usual way yielded 6·3 g. of viscous material which proved to be unchanged oil, and 2·3 g. of impure acid possessing an acrid odour. The volatile products of ozonolysis proved to contain formaldehyde which was identified by preparations of 2:4-dinitrophenylhydrazone and the dimedone derivative (m.ps. 166° and 189° respectively).

Fraction X.—This sesquiterpene fraction when treated with hydrogen chloride gave red or purple oils which did not crystallize. The lower boiling fractions of the hydrochlorides, b.p. 95–102°/2 mm. gave molecular refractivities characteristic of monohydrochlorides, while the higher boiling portions of the fraction contained traces of azulene and the molecular refractivities of the hydrochlorides approached those of dihydrochlorides.

Selenium dehydrogenation.—The lower boiling portion of the fraction (4 g.) mixed with selenium (3 g.) was heated in a pyrex tube and the temperature maintained at 275° for twenty hours. The cooled reaction mixture was extracted with ether and on distillation yielded unchanged oil, guaiazulene (characterized as the 1:3:5-trinitrobenzoate) and tarry material. No naphthalene homologue could be isolated. Attempts to prepare crystalline nitrosochloride, nitrosate, nitrosite and bromide failed, but on addition of bromine azulene was obtained.

Fraction XI was treated with hydrogen chloride and yielded a green viscous oil which distilled at 105–115°/2 mm. The molecular refractivity was that of dihydrochloride.

On selenium dehydrogenation it yielded guaiazulene (a trace), cadalene (picrate m.p. 116°), and some tarry residue.

No other crystalline derivatives could be obtained from this fraction.

The residue which distilled at 285–320°/760 mm. consisted apparently of a mixture of sesquiterpene alcohols and diterpenes. No crystalline material separated after long standing and was not further investigated. The intense blue colour of this residue suggested the presence of azulene which, when extracted by Sherndal's method, could not be crystallized even by immersion in liquid air. The preparation of a picrate, m.p. 122·5°, and a 1:3:5-trinitrobenzoate, m.p. 151°, confirmed its identity as guaiazulene which is present in the oil to the extent of 0·03%.

The paraffins—From the residue from fractionation, extraction with hot alcohol yielded a small amount of solid paraffin, m.p. 62°. This is probably an impure mixture which distilled over a range of temperature from 382° to 425° at 760 mm. pressure.

Conclusion

The oil of *P. tenuifolium*, the chief constituent of which is *d*-α-pinene, offers a striking contrast to that of *P. eugeniodes*, the main portion of the latter oil consisting of *n*-nonane.

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Department of Chemistry
University of Otago
Dunedin

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SALTY FLAVOUR IN BACON

By M. INGRAM

The flavour of bacon is usually much less salty than would be expected on the basis of the salt-content. This is expressed by an "availability index" which is the ratio of the salty flavour observed, to that of a solution containing the same percentage of salt as the bacon, reckoned on fresh weight. The availability index seems to be an expression of the muscular structure, since it is similar in symmetrical pairs of muscles on opposite sides of a pig, and is largely independent of the quantity of salt added to the meat. Because the availability increases with juiciness, it is suggested that the intensity of salty flavour depends on the speed at which salt is liberated in the mouth on chewing bacon. Juiciness increases with decreasing p_H in muscles; hence the availability of salt increases with acidity in bacon. A bacon of p_H 6·2 might perhaps contain twice as much salt as one of p_H 5·3, without tasting more salty. Besides the p_H, other characters such as toughness are probably involved.

Introduction

The salt which is added to bacon as a preservative also contributes a flavour. In old-fashioned bacon, which was intended to keep for a very long time without any special precaution, so much salt had to be added as to make the bacon excessively salty, but with the development of refrigeration as an aid in preservation, and more rapid distribution, the addition of so much salt has gradually become less necessary, and public taste has moved towards a less salty product. In 1940, for example, a survey in this country revealed that the flavour of imported bacon, both Danish and Canadian, was on the whole too salty for British taste.[1] Considerable importance therefore attaches

to the factors influencing salty flavour, and this account describes a short investigation, begun in 1940–42, but interrupted by the war.

Methods

As the fat contributes little to the salty flavour of bacon, attention was confined to the lean portions of ordinary cuts, or to muscles (e.g. *psoas*) which include no fatty tissue. To estimate the organoleptic qualities a tasting panel was set up, composed of five persons with considerable experience in tasting bacon and various curing solutions. Samples were fried in fresh lard for a standard time in a gas griller; and were then tasted under code at random, except that a very salty sample was not tasted immediately before a sample containing much less salt. The panel awarded marks according to the following scale:

Score	Salty flavour	Juiciness	Texture
0	Nil		
1	Perceptible	Dry	Very tough
2	Slight	Rather dry	Rather tough
3	Moderate	Normal	Normal
4	Marked	Rather juicy	Rather tender
5	Very strong	Very juicy	Very tender

All the tests were made with material at room temperature (*ca.* 18° C.).

The salt was estimated on minced mixed samples of about 100 g. weight by electrometric titration with silver nitrate,[2] and expressed as g. NaCl/100 g. meat, or solution. Dry weights were determined on *ca.* 20 g. samples of the same mince, dried on a water-bath and finished for 24 hours. at 105° C.

Results

The tests revealed at once that the salty flavour of bacon depends largely on factors additional to the salt-content, to which it does not bear any very direct relation. Observations are presented in Fig. 1. It is true, of course, that, in general, the more salt the stronger the flavour; but bacon with 5% salt, for example, might taste very salty, or hardly salty at all.

The second striking feature was that the bacon was almost always less salty, often very much less, than a salt solution of corresponding concentration. (See Fig. 1.) This feature is

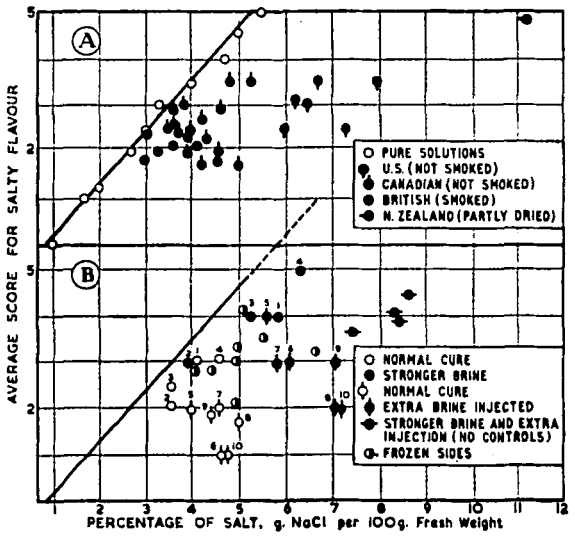

FIG. 1. *Salt-content and salty flavour of bacon, compared with that in salt solutions*

(*a*) *Normal commercial bacons*
(*b*) *Experimentally cured bacon—the numbers indicate corresponding paired sides, in one of which the salt-content was unduly increased by hard curing*

the more remarkable, in that the salt concentrations in Fig. 1 are reckoned on the basis of fresh weight, of which only about 75% is water, so that the actual concentrations of salt in solution might be expected to be greater by about one-third than those shown, and the salty flavour stronger instead of weaker. As the salty flavour rarely equals that of a corresponding solution even on the basis of fresh weight, and has never been observed to exceed it, it seems likely that the solids of the bacon also act as diluents to the salty flavour; so that the salt-concentration in the meat is better stated in terms of fresh weight, as has been done here, rather than in terms of water-content.

One can only suppose that some of the salt in the bacon is for some reason not available to be tasted. This can be expressed by the use of an "availability index," calculated as the ratio between the salty flavour score of a bacon and that of a solution of the same salt concentration. This procedure seemed reasonable since, in the range in which we were interested, the salty flavour score of solutions increased roughly in proportion to their concentration. The availability index, which has varied between 1·0 and 0·2, is apparently related to the structure of the muscle as there is a correlation between the values obtained in similar muscles on opposite sides of an animal. Fig. 2A shows this for paired *psoas major* muscles, cured in acid brines of the same salt-content and p_H but with different acids.* A still more striking case is illustrated in Fig. 2B, where the points represent cuts from the *longissimus dorsi* in paired sides, one of which was cured normally while the other had its salt-content considerably increased by extra pumping or the use of stronger brine (the basic observations are given in Fig. 1B). It appears from Fig. 2B that the ratio of salty flavour to salt-content was on the whole preserved, although the salt-content was considerably increased, i.e. it depends on some property of the muscle, shared by paired muscles in the same animal.

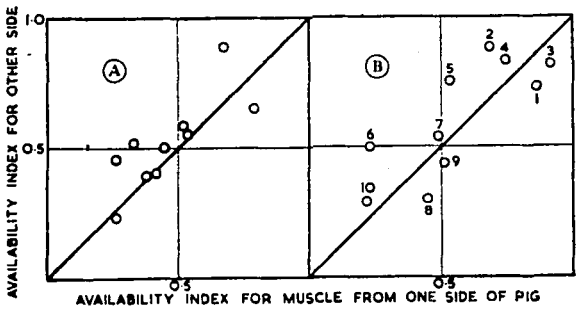

FIG. 2. *Correlation between the availabilities of salt in paired muscles from opposite sides of the pig:*

(*a*) Psoas major *muscles—compared after curing members of pair in different brines of same* p_H *and salt content*
(*b*) Longissimus dorsi *muscles—compared after curing one side normally and the other with extra salt (the numbers indicate the pairs in Fig. 1b)*

Callow has shown[4] that the electrical resistance of a suspension of meat in salt solution is, in a similar manner, less than can be accounted for on the basis of the salt present; which means that, as with flavour, a part of the salt is not available.

Callow found further that the discrepancy increased with the salt-content, and supposed that this was because the salt made the structure of the meat less "open." In this case, the availability index in a hard-cured side should be on the average lower that in a corresponding normally-cured side. There is no evidence of such a relation in Fig. 2B, but the observations are rather few to demonstrate such a difference, which would be small, since trebling the salt-content of minced muscle apparently

*These observations were made during a separate investigation,[3] which showed that the effects of the different acids were indistinguishable at the same p_H and salt-concentration, so the variations in Fig. 2A may be ascribed to peculiarities of the muscles themselves.

changed the proportion (not, of course, the *absolute* amount) of available salt by only about 4% (cf. (4), Fig. 2).

It seems evident that if the salt were dissolved in the water of the bacon, and this were quite free, the salt would be completely available. This state is never completely realised, but it would likewise be expected that the more juicy the bacon, the more freely the salt should be available (other things being equal), which proves to be the case (Fig. 3): the "availability index" is high in bacon which is juicy. It is plain that it is only that part of the water available as juice which is effective in carrying the salty flavour, for there is no evident relation between the *total* quantity of water in the bacon and the production of the

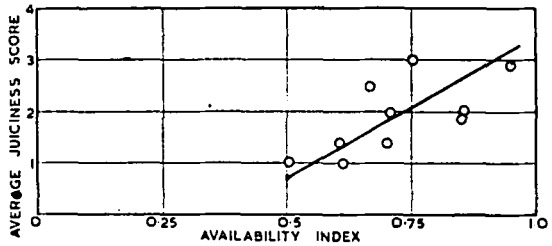

FIG. 3. *Correlation between juiciness and availability of salt in samples of normal bacon*

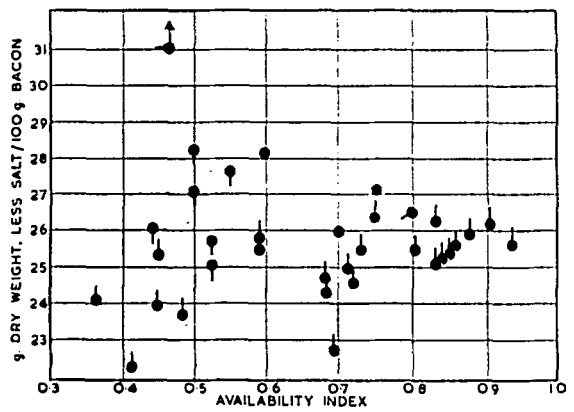

FIG. 4. *Absence of correlation between water-content of bacon and availability of salt in it. (Symbols as in Fig. 1a.)*

salty flavour (Fig. 4). It is evident that the salty flavour can arise only from that part of the salt which is available in the mouth, and it follows that the intensity of the flavour depends on the speed with which the salt is set free in the juices on being masticated.

There is a property of lean meat by virtue of which the quantity of free fluid in it can change without corresponding change in total fluid: this is the p_H. There is, moreover, a very close similarity between the p_H values of paired muscles on opposite sides of an animal (e.g., Fig. 5), though there may be occasional exceptions. Callow has shown how acid muscles (p_H about 5·5) have an "open" structure, in which there is free fluid between widely-separated fibrils, in contrast with relatively alkaline muscles (p_H 6·0–6·5) where the fluid is imbibed into the fibrils, and the structure is "closed." In particular, he has demonstrated that salt and sugar penetrate more freely into acid muscle of "open" structure[5] and it therefore seemed reasonable to expect, as has since been found, that salt might be more freely available for tasting in the open structure of relatively acid meat (Fig. 6).

The effect of p_H may be very important quantitatively, for Fig. 6 suggests that salt would be roughly twice as freely available in an "acid" muscle as in an "alkaline" one, i.e., the latter could have twice as much salt without tasting more salty.

It is possible that other properties of the muscle, in addition to p_H, may influence the availability of the salt. This is suggested, for example, by the way in which *both* muscles, of the pairs represented by numbers 1 and 5 in Fig. 6, stand together rather apart from the general p_H/flavour relation. A property of the kind which might be involved is the toughness due not to p_H but to factors such as age and nutrition; the tougher the meat, the less easy it is to masticate out the salty juice. We

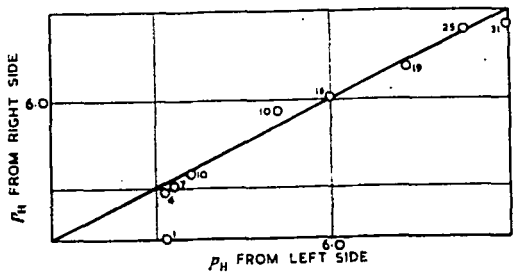

FIG. 5. *Close correlation between p_Hs of opposite members of pairs of* psoas major *muscles from the same animal (points 1–16 represent averages of groups of 3 pairs, 19–31 groups of 6 pairs)*

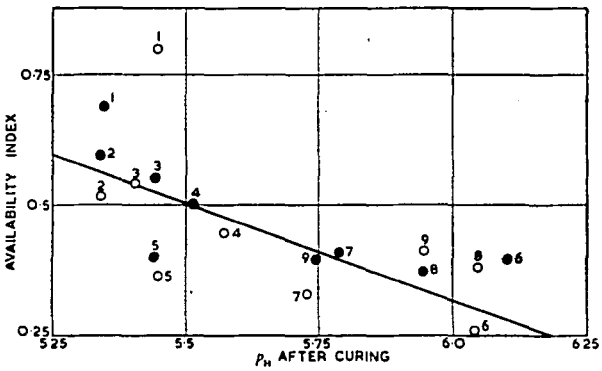

FIG. 6. *Correlation between the acidity of experimentally-cured pork and the availability of salt in it. (Numbers indicate paired* psoas major *muscles from the same animals)*

have in fact observed some indication of a rough inverse relation between toughness and availability of salty flavour (Fig. 7). (In these experiments the factors responsible for the toughness were not analysed, but the variations were not due to variations in water-content, since this was about the same in all the samples represented; it is important that this source of variation should be eliminated, for it will be obvious that toughness caused by drying would be accompanied by increased saltiness.) Again, if the meat is frozen before curing, the structure is much more open, and it takes up salt much more readily[6]: hence the salt should be more readily available than normal in the resulting bacon, and the observations we have so far made support this view (Fig. 1B) though they are too few to demonstrate it clearly.

Discussion

The suggestions made above help in appreciating differences between different "styles" of bacon, for example between those in Britain and the U.S.A. The British taste is for a rather lean bacon and, because the desire for mild cures has emphasised the necessity for resting the pigs before slaughter, this bacon

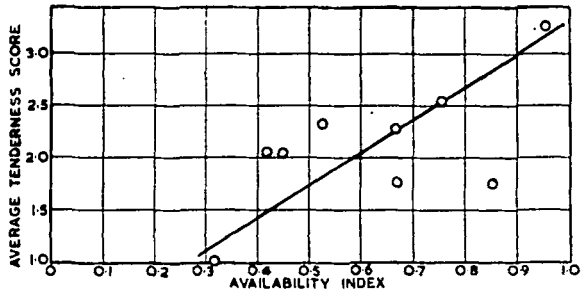

FIG. 7. *Possible inverse correlation between toughness and availability of salt in samples of normal bacon*

is relatively acid, the p_H averaging 5·6–5·7.[7] The U.S. pig is fatter, older, and therefore tougher, and is not as a rule rested before slaughter, so that the bacon from it is probably less acid, the p_H perhaps averaging about 6.[8] The results of the few comparisons made indicate that there is a corresponding difference in the availability of the salt, such that U.S. bacon does not taste markedly more salty than British (see Fig. 1A), although it contains considerably more salt. Canadian bacon is apparently intermediate between the two.

Acknowledgment

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Low Temperature Station for Research in Biochemistry and Biophysics,
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THE ESSENTIAL OIL OF *LIBOCEDRUS BIDWILLII*—NEW ZEALAND CEDAR

By R. D. BATT and C. H. HASSELL

The application of a highly efficient fractionating column to the analysis of essential oils has been studied through the use of a spiral gauze column in the re-examination of the essential oil of Libocedrus bidwillii (New Zealand Cedar). The following fifteen constituents have been separated. *l*-α-pinene (24·8%); *d*-sabinene (3·3%); myrcene (2·7%); ketone ($C_{10}H_{16}O$) (3·7%); limonene and dipentene (7·4%); *p*-cymene (3·4%); terpinolene (0·7%); terpinen-4-ol (1·2%); unidentified tricylic sesquiterpene (1·6%); unidentified sesquiterpene (3·7%); caryophyllene (3·0%); γ-curcumene (18·4%); *d*-cadinene (2·7%); green oil (5·8%); and tar (including hydrocarbon) (8·2%).

Except in the case of simple mixtures, the difficulty involved in separating the closely related constituents of essential oils by simple fractional distillation has rendered their analysis tedious and of uncertain accuracy. It appeared that these disadvantages could be largely overcome by the use of a suitable fractionating column with an efficiency of approximately 40 theoretical plates. This view has been confirmed in the analysis of the complex essential oil of the New Zealand cedar, *Libocedrus bidwillii*.

The essential oil of the leaves of *Libocedrus bidwillii* was first examined by Gourdie[1] who characterized *d*-α-pinene. In a further examination of the oil Birrell[2] identified α-pinene and also suggested the presence of β-pinene, limonene and dipentene, an unidentified sesquiterpene and probably a white, solid diterpene, m.p. 53–55°. The analysis was rendered incomplete however[3] by the difficulty found in separating the constituents by fractional distillation under reduced pressure.

Of the eight related Libocedrus species only *L. decurrens* has been investigated. The essential oil was found to contain α-pinene, sylvestrene, *d*-limonene, dipentene, borneol, bornyl acetate and a new sesquiterpene.[4]

The autumn oil of *L. bidwillii*, obtained in 0·29% yield by steam distillation of leaves and terminal twigs, was fractionated under reduced pressure using a 91 cm. vacuum jacketed fractionating column similar to that described by Lecky and Ewell.[5] It had an efficiency under total reflux equivalent to 39 theoretical plates. This spiral gauze type of fractionating column has low H.E.T.P., low hold-up, low pressure drop and simple construction and operation characteristics that recommend it for use in the distillation of essential oils.

In the course of the distillation of intermediate fractions the throughput was decreased while the reflux ratio remained constant.[6] The progress of the fractionation is indicated in the distillation curves in Fig. 1.

Physical constants of the purest samples of the fractions are shown in Table I in comparison with what appear to be the best authenticated values of the known compounds with which they have been identified. The identity of the fractions was indicated by a comparison of physical constants and addition and degradation products.

In the terpene range *l*-α-pinene (24·8%), *d*-sabinene (3·3%), myrcene (2·7%), limonene and dipentene (7·45%), *p*-cymene (3·45%) and terpinolene (0·7%) have been characterized. These compounds have been isolated already from the essential oils of related species of *Cupressaceae*.[7] However, the compound $C_{10}H_{16}O$ (fraction 4), b.p. 56·2/10 mm., R_D 49·36, does not appear to have been described before. The ultra-violet absorption spectrum in *cyclo*hexane, λ max. 2657 A (log ε max. 3·23) and molecular refraction are consistent with its formulation as an acyclic carbonyl compound with conjugated olefinic linkages (R_D calc., 47·46). It gives colour reactions with *m*-phenylenediamine hydrochloride, sodium nitroprusside and dinitrobenzene characteristic of carbonyl compounds and reacts with 2 : 4-dinitrophenylhydrazine to give an unstable derivative. These properties differentiate it from the known acyclic terpenoid ketones tagetone[8] and artemesia and isoartemesia ketone.[9] As in the case of other essential oils containing sabinene, the hydration product terpinen-4-ol was also isolated from the imixture.

Of the higher boiling constituents, caryophyllene and *d*-cadinene were identified. Both of these compounds have been isolated previously from species of the *Cupressaceae*.[7] The tricyclic sesquiterpene (fraction 9) and also fraction 10 have not been characterized. Neither fraction gave crystalline derivatives and in the latter case, unlike aromadendrene,[10] no solid product was obtained on ozonolysis.

The main sequiterpene constituent, fraction 12 (18·4%), does not appear to have been isolated previously. As a result of investigations on the structure of this compound,[11] it has been named γ-curcumene. The green oil (fraction 14) which is the least volatile component gives colour reactions with bromine and acetic anhydride sulphuric acid similar to those of the green oil obtained by Schorger[1] from *L. decurrens*.

The residue remaining on distillation of the essential oil was recrystallized to yield a white hydrocarbon, m.p. 56–56·5°. This product showed no unsaturated properties on treatment with tetranitromethane and bromine solutions. It was therefore