Chemistry of Fruit-flies. Spiroacetal-rich Secretions in several *Bactrocera* species from the South-West Pacific Region

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The male rectal glandular secretions from the fruit-fly pest species *Bactrocera* (*Notodacus*) *xanthodes* (Broun) and *Bactrocera* (*Bactrocera*) *kirki* (Froggatt) and the non-pest species, *Bactrocera* (*Bactrocera*) *kraussi* (Hardy) are rich in spiroacetals. In *B. xanthodes*, (5*R*,7*S*)-7-methyl-1,6-dioxaspiro[4.5]decane is prominent, whereas in *B. kirki* (2*S*,6*R*,8*S*)-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane is the single major volatile component. *B. kraussi*, although rich (~40%) in (2*S*,6*R*,8*S*)-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane, contains other spiroacetals and a number of compounds that may be biosynthetically related to the spiroacetals. The absolute configurations have been determined by enantioselective syntheses and chiral gas-chromatographic determinations. The results of examinations of *Bactrocera* (*Bactrocera*) *passiflorae* (Froggatt) and *Bactrocera* (*Bactrocera*) *facialis* (Coquillett) are also reported.

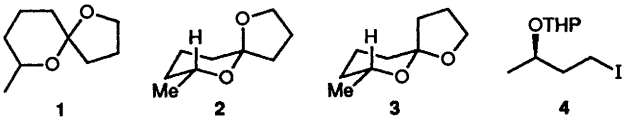
Increasing attention is being directed to the use of pheromone-based attractants for Tephritid fruit-fly species, which are a scourge of horticulture in many parts of the tropical and temperate world.[1] This emphasis is justified because considerable progress has been made in fruit-fly chemistry,[2–8] particularly with respect to the components of (male) rectal glandular secretions and associated volatile emissions that are implicated in the mate-finding and mating processes. In a parallel way, impressive strides have been taken in understanding general fruit-fly biology and taxonomy.[9] Although most effort has focussed on species having pest-status, studies of non-pest species are also worthwhile so that panoramic understanding of these insects will result, with appreciation of the chemistry and biochemistry involved at various stages of the life-cycle. This will permit the most efficient intervention for control purposes.[10]

As part of a general programme in this area, we have reported studies of a variety of Tephritid fruit-fly species, principally derived from the genus *Bactrocera*,† and remarked on the chemical diversity and apparently varied biosynthetic routes utilised by these species.[5] Alkyl spiroacetals are prominent components of a number of male fruit-fly secretions and volatile emissions,[2–7] and there is evidence[7] of their importance in behaviour mediation. Here, we extend our previous examinations and report that spiroacetals are very prominent components in the rectal glandular secretions of three unrelated species from different locations in the South-West Pacific region. These species are *Bactrocera* (*Notodacus*) *xanthodes* (Broun), *Bactrocera* (*Bactrocera*) *kirki* (Froggatt) and *Bactrocera* (*Bactrocera*) *kraussi* (Hardy). In addition studies of *Bactrocera* (*Bactrocera*) *passiflorae* (Froggatt) and *Bactrocera* (*Bactrocera*) *facialis* (Coquillett) have also been undertaken.

Results and Discussion

B. xanthodes[9] is distributed throughout Fiji, Western Samoa, Tonga, Cook Islands and Vanuatu and has been bred from pineapple, citrus, papaya, guava and tomatoes, and watermelon has been identified as a newer commercial host. This species has the potential to become a very serious pest in areas of intensive horticulture, and already causes severe crop losses in areas where subsistence horticulture is practised, and control measures are rudimentary. Twelve pentane extracts of *B. xanthodes* male glands were obtained from various locations in the South Pacific, and examined by GC–MS methods, using non-polar columns. All samples from young mature flies (1–4 weeks) contained only two relatively volatile components in a 20:1 ratio, each with an apparent molecular weight of 156, and an ion at *m/z* 141, corresponding to methyl group loss. Prominent ions were observed at *m/z*, 84, 87 with smaller ions at *m/z* 97, 112 and 115. Such fragmentation patterns are indicative[11] of a spiroacetal struture and specifically 7-methyl-1,6-dioxaspiro[4.5]decane **1**,[11b] with the isomers being the anomerically stabilised *E*-isomer **2** and the less-abundant *Z*-arrangement **3**, respectively.

These conclusions were confirmed by GC–MS examination and co-injection of authentic, synthesised samples of (±)-**2** and (±)-**3**. These were acquired by sequential alkylations of anions derived from *N*,*N*-dimethylacetonehydrazone[12] with 3-(tetrahydropyranyloxy)-1-iodobutane and ethylene oxide, followed by hydrolysis, deprotection, and cyclisation (Scheme 1).‡ Use of



1 **2** **3** **4**

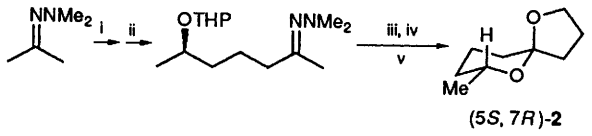
chiral iodide **4**[13,14] in the synthesis resulted in acquisition of (5*R*,7*R*)-**2** which exhibited $[\alpha]_D^{22}$ +84.0° (*c* = 2.2, pentane) which compares well with that for an alternatively synthesised sample {$[\alpha]_D^{22}$ +87.8° (neat)}.[15] The (5*S*,7*S*)-isomer exhibits $[\alpha]_D^{20}$ −78.2° (neat),[16] and $[\alpha]_D^{22}$ −78.3° (pentane).[17] Chiral GC examination utilising a Lipodex A column showed the synthesised sample to possess an enantiomeric excess (ee) of at least 98%, and to elute prior to its antipode.§ Analysis of the *B.*

† *Bactrocera* is the new genus name applied in the general taxonomical revision[9] to a large number of fruit-fly species previously located in the *Dacus* genus.

‡ For a similar sequence see ref. 5.

§ This order of elution has been observed[16] with nickel(II) and manganese(II)–bis-3-heptafluorobutyryl-1*R*-camphorate phases.

xanthodes sample confirmed (5*S*,7*S*)-**2** to be the natural product with an ee of 95%. As far as we are aware, isomers of **1** have not previously been detected in fruit-fly species, but (5*S*,7*S*)-**2** has been identified in *Conophthorus* bark-beetles, in pine-bark beetles *Cryphalus piceae*, in the ash bark beetle *Leperisinus varius* and in common wasps, *Paravespula spp.*[18] A recent report[15] established (5*S*,7*S*)-**2** (95–97% ee) as a component of the volatiles produced by males of jack pine tip beetle, *Conophthorus banksianae* (McPherson) and two related species.



(5*S*, 7*R*)-**2**

Scheme 1 *Reagents and conditions:* i, BuLi (1.05 equiv.), THF, −78 °C, 1.5 h; ii, Iodide **4** (1.05 equiv.), −78 → 20 °C, 15 h; iii, BuLi (1.05 equiv.), −78 → 20 °C, 4.5 h; iv, $\overline{OCH_2CH_2}$ (1.2 equiv.), −78 → 20 °C, 48 h; v, 2 mol dm^{-3} HCl, 20 °C, 0.3 h

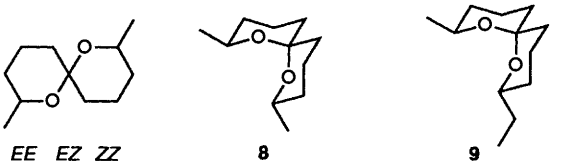
Components of lower volatility than **1**, were also present in the extracts of young, mature *B. xanthodes*. Acetates of saturated and unsaturated C_{16}, C_{18} and C_{20} fatty alcohols were prominent. Comparison of mass spectra and co-injection of synthetic and commercial samples indicated the presence of hexadecanyl acetate, octadecanyl acetate, *cis*-octadec-11-enyl acetate, *cis*-octadec-9-enyl acetate, eicosanyl acetate, *cis*-eicos-11-enyl acetate and *cis*-eicos-13-enyl acetate. Long chain hydrocarbons were also present and consisted of two major components (*ca.* 3:1) with many minor components which were not positively identified. The larger component, on the basis of mass spectral behaviour, was considered to be an unsaturated C-29 hydrocarbon and the presence of a C-9 double bond was confirmed by dimethyldisulfide addition, followed by GC–MS analysis.[19] Comparison of our calculated linear retention index[20] with literature values[21] confirmed the identity of nonacos-9-ene. Mass spectral data indicated the smaller component was a mixture of 11-, 13- and 15-methylnonacosane, and this conclusion was supported by comparison of our linear retention index with literature values.[21] In addition, our mass spectra of these two major hydrocarbon components correlated well with unpublished mass spectra[21] of authentic samples of these hydrocarbons.

There was considerable variation in the proportions of spiroacetal **1**, fatty alcohol acetates and long-chain hydrocarbons present in the *B-xanthodes* extracts. This variation appeared to be more dependent on the age of the flies, rather than their source. Glandular extracts from flies older than four weeks obtained from Fiji, Tonga and the Cook Islands contained only the hydrocarbons. Extracts from younger flies obtained from the same sources consistently contained spiroacetal **1** and fatty alcohol acetates, but the level of hydrocarbons varied from absence to being the major components.

B. kirki is a medium-sized species that is widely distributed in the South Pacific Islands of Western and American Samoa, Tonga, Niue Island and Tahiti and has been bred from peach, mango, guava and capsicum.[9] It is a destructive pest of commercial and small-scale horticulture in these islands. The rectal gland extract of male *B. kirki* obtained from Tonga contained a single major component on the basis of GC–MS examination. This component was shown to be (*E*,*E*)-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane **5**[22,4] by mass spectral and chromatographic comparisons (co-injection) with an authentic sample. Furthermore, this spiroacetal was highly enantiomerically pure (ee at least 95% chiral gas-chromatography, Lipodex A column), possessing the (2*S*,6*R*,8*S*)-configuration **8** as already established for this component in *B. cucumis* and *B. nigrotibialus*.[23] Minor compounds were identified as (*E*,*Z*)-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane **6**[22,4] and (*E*,*E*)-2-ethyl-8-methyl-1,7-dioxaspiro[5.5]undecane **9**,[4,23,24] by chromatographic and mass spectral comparisons with authentic samples. Although the absolute stereochemistry of **9** is not known in the present case, it is likely to be (2*S*,6*R*,8*S*) (as drawn for **9**), on the basis of our determination for this component in *B. nigrotibialus*.[23] In view of the pest-status of *B. kirki* and the almost single component nature of the male glandular secretion, a control measure based on **5** or **8** as a lure may be feasible.

B. kraussi is a medium sized species in the *fagraea* complex of flies and has been recorded from rainforests along the North-Eastern Queensland coast and Cape York.[9] It is closely related to *B. halfordiae* (Tryon) and occupies the host niche in North Queensland that *B. halfordiae* occupies in South-East Queensland.[9] *B. kraussi* is not an economic pest and infests only rainforest fruit. The rectal gland extract consisted of one major (~40% of volatiles), six significant (2–13%) and five minor (> 1%) components. The dominant component was (*E*,*E*)-2,8-dimethyl-1,7-dioxaspiro[5.5]undecane[4,22] with the (2*S*,6*R*,8*S*)-configuration **8** (ee of at least 98%, Lipodex A column). In view of the taxonomic and host similarity, this same configuration almost certainly applies to this spiroacetal from *B. halfordiae*,[4] in which it is the major (70%) component.

Four of the less abundant compounds in *B. kraussi* were spiroacetals. (*E*,*E*)-2-Ethyl-8-methyl-1,7-dioxaspiro[5.5]undecane **9**[4,23,24] (of unestablished chirality), and an isomer of



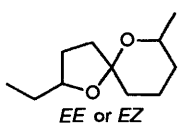
EE *EZ* *ZZ*
5 **6** **7**

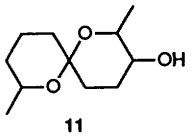
8 **9**

2,8-dimethyl-1,7-dioxaspiro[5.5]undecane were significant. This latter spiroacetal exhibited a mass spectrum similar to that for the (*E*,*Z*)- and (*Z*,*Z*)-isomers, **6** and **7** respectively, but a retention time longer than that for the authentic (*E*,*Z*)-isomer **6**. On this basis, the (*Z*,*Z*) arrangement **7** is assigned.[4] This diastereoisomer is known to co-occur with the (*E*,*E*)- and (*E*,*Z*)-isomers in *B. cucumis* for example,[4] and full characterisation of this interesting spiroacetal has been presented.[4] A minor component was identified as (*E*,*E*) or (*E*,*Z*)-2-ethyl-7-methyl-1,6-dioxaspiro[4.5]decane **10** based on mass spectral[11b] and chromatographic comparisons with synthesised (*E*,*E*)- and (*Z*,*E*)-isomers, the configurations of which were established by NMR studies.[25] A further minor component was tentatively identified as 2,8-dimethyl-1,7-dioxaspiro[5.5]undecan-3-ol **11**,[4,14] (based on GC–MS behaviour), which is known to co-occur with **5**, **6** and **7** in *B. cucumis*.[4]

Three components that could be related biosynthetically to spiroacetals were also observed. 9-Hydroxynonan-4-one **12**,[4,24] was a significant component and was identified by GC–MS and chromatographic identity with a separately synthesised sample.[26] 2-Methyl-6-pentyl-3,4-dihydro-2*H*-pyran **13**[27] and its open chain, hydrated form, 2-hydroxyundecan-6-one **14** were tentatively identified as minor and significant components respectively. Synthesis of **14** was carried out by sequential alkylation of acetone–dimethylhydrazone[12,*] in a manner similar to that shown in Scheme 1. Thus alkylation with (±)-**4** and then with butyl bromide, followed by hydrolysis and deprotection led to a mixture of **14** and hemiketal **15** (*ca.* 5:1),

* For a similar sequence see ref. 5.


EE or EZ
10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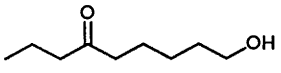
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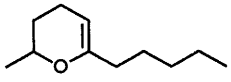
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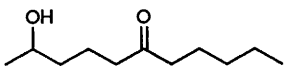
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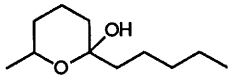
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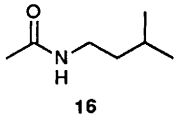
which was purified by preparative HPLC. Preparative gas chromatography of this mixture led to dihydropyran **13** by dehydration of **15**. Use of (*R*)-**4** in the sequence provided (*R*)-**13** which exhibited $[\alpha]_D^{22} = +45.45$. Because of the interconvertibility and dehydration of **14** and **15** to **13**, no attempt was made to obtain pure samples of (*R*)-**14** and (*R*)-**15**. In any event, keto alcohol **14** was not separated into its enantiomers either as its trifluoroacetate on Lipodex A or underivatised on β-cyclodextrin columns. Hemiketal **15** does not survive gas chromatography and consequently, its status as a glandular component is uncertain. However, the dihydropyran (±)-**13** was nicely separated into its enantiomers on a β-cyclodextrin column, and synthesised (*R*)-**13** exhibited an ee of at least 97%. With these samples available, **13** and **14** were confirmed as significant natural components. Analysis of (±)-**13**, (*R*)-**13** and the glandular secretion confirmed natural **13** to be the (*S*)-enantiomer, with an ee of 95%. Because of the structural relationship between **13** and **14**, the latter is also assigned the (*S*)-configuration. This same configuration is present in the related spiroacetal **8**. Dihydropyran **13** occurs also in *B. halfordiae* and here it is likely to be the (*S*)-enantiomer also.* Other components present in *B. krausi* extracts included amides **16** and **17**, identified previously in other fruit-fly species,[3,28] and confirmed by mass spectral and gas chromatographic comparisons with authentic samples, with **16** being more abundant than **17**. 3-Methylbutanol **18** and diethyl succinate **19** were minor constituents.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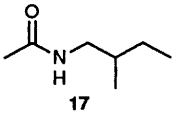
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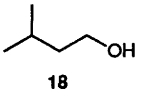
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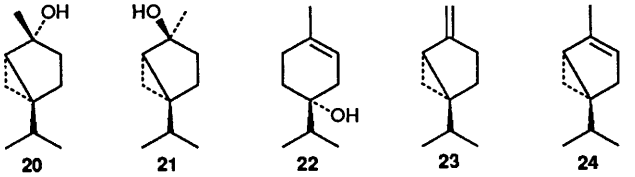
19

Examination of the volatile emission from male *B. kraussi* were also conducted, and spiroacetal **8** was the major constituent of the volatiles trapped on activated charcoal. Amide **16**, keto alcohol **14** and 3-methylbutanol **18** were also identified. There is a close similarity between *B. kraussi* and *B. halfordiae* with respect to their glandular secretions, with (*E,E*)-**5**, **9**, **10**, **12** and **13** being common to these species. However, in our examination of *B. halfordiae* we detected only the (*E,E*) isomer of 2,8-dimethyl-1,7-dioxaspiro[5.5]undecane **5**, whereas the (*E,E*)-**5** and (*Z,Z*)-isomers **7** occur in *B. kraussi*.

B. passiflorae[9] has been recorded from Fiji and Tonga and is known to infest citrus, passionfruit, mango and granadilla. Similarly *B. facialis*[9] infests a range of fruits and vegetables including citrus, peach, mango, capsicum and tomato, with the potential to become a major pest if introduced into areas of intense horticulture. This species has been recorded from Tongatapu island and the Ha'apai group in Tonga,[9] but is probably widespread in the Tonga islands.

Three extracts of *B. passiflorae* glands from a laboratory colony reared on a pawpaw based diet contained a single major component, whose mass spectrum matched library spectra of *cis*/*trans*-thujan-4-ol **20** and **21**. An authentic sample containing *cis*- and *trans*-thujan-4-ol **20** and **21**, and terpinen-4-ol **22** was kindly provided by Dr I. Southwell, and co-injection studies demonstrated that the major component in *B. passiflorae* was *cis*-thujan-4-ol **20**. Three other components were present at significant levels, and one exhibited a mass spectrum essentially identical with that of the major component **20**, and co-eluted with *trans*-thujan-4-ol **21**. The other significant components


20 21 22 23 24

were identified by mass spectral and GC comparisons as terpinen-4-ol **22** and *N*-3-methylbutylacetamide **16**. A number of very minor components were also observed, and four of these have been tentatively identified (mass spectral library matching) as sabinene **23**, α-terpinene, δ-terpinene and Δ^3-carene. Three pyrazines were also present and corresponded very closely in mass spectra with 2,5 (or 6) dimethylpyrazine, 3-ethyl-2,5-(or 6)-dimethylpyrazine and 2,5 (or 6)-dimethyl-3-propylpyrazine. Gland extracts from *B. passiflorae* bred from field-collected rose-apple (*syzygium jambos*) contained less volatiles, with the major component being terpinen-4-ol **22**. Terpinen-4-ol **22** has been reported as a component of *Syzygium jambos* volatiles.[29]

Two *B. facialis* gland extracts from flies reared on a similar pawpaw based medium contained the same single major component **20**, and three minor components, **21**, **22** and **16**. These two species of fruit-fly are unrelated and the terpenes observed are believed to be diet-related, as pawpaw pulp contains sabinene **23** among other terpenes.[30] These components were not observed (see above) in the glandular extracts of *B. xanthodes*, *B. distincta* and *B. kirki* which had been reared on similar media. However, terpenes and pyrazines have been identified previously from male rectal gland extracts of a number of Tephritid fruit-fly species.[26a,31] Interestingly, terpinen-4-ol **22** is an aggregation pheromone of the European spruce bark beetle, *Polygraphus poligraphus*, and is thought to arise from the host terpenes sabinene **23** and α-thujene **24**.[32,33] The 4-thujanols **20** and **21** have also been detected in *P. poligraphus* hindguts and are proposed intermediates in the conversion to terpinen-4-ol **22**.[32] The bioconversion of sabinene **23** into terpinen-4-ol **22** and α-terpineol by the bark beetle, *Phloeosinus armatus*, has also been reported and is believed to involve bacteria in the hindgut of this beetle.[34] In *B. passiflorae* and *B. facialis* the role of the host terpenes and their oxidation products **20**, **21** and **22** is unclear and warrants further investigation.

The present findings when coupled with existing data confirm the widespread occurrence of spiroacetals in fruit-flies located in diverse parts of tropical and temperate regions. The established[7] behaviour-mediating role for 1,7-dioxaspiro-[5.5]undecane in the olive-fly (*B. oleae*) indicates the likelihood of similar roles for spiroacetals in other species but the generality of this remains to be demonstrated. In addition, the wide variety of organic compounds identified from Tephritid species discloses a remarkably versatile biosynthetic capability for these fascinating but often destructive insects. In this context, the demonstration of a very predominent component

* The occurrence of **13** in other insect species is outlined in ref. 4.

in the male rectal gland secretion (*e.g. B. kirki*) and volatile emission is encouraging from a control viewpoint. We hope to report on this aspect in the near future.

Experimental

Spectra.—^{1}H NMR spectra were recorded at 400 MHz (FT mode) on a JEOL JNM-GX 400 spectrometer and deuteriochloroform was employed as solvent. Chemical shifts (δ values) are relative to internal tetramethylsilane (δ 0.0) or residual $CHCl_3$ (δ 7.24). ^{13}C NMR spectra were recorded at 100 MHz, again with deuteriochloroform as solvent and chemical shifts are relative to the central component of the $CDCl_3$ triplet at δ_C 77.00, J values are given in Hz. Low resolution mass spectra refer to combined GC–MS measurements recorded on a Hewlett-Packard 5970 Series GC–MS system, using a non-polar (BP5) column, or a Finnigan Mat 1020 GC–MS system. Optical rotations were recorded using a Perkin-Elmer 241 MC polarimeter, $[\alpha]_D$ values are given in 10^{-1} deg cm^2 g^{-1}. Chiral gas chromatographic analyses were conducted using a Lipodex A 50 m column (Macherey–Nagel) and a CP-cyclodextrin-β-2,3,6,-M-19 50 m column (Chrompack). Linear Retention Indices of long chain hydrocarbons were determined on a BP-1 column (non-polar) at 220 °C programmed at 5 °C min^{-1} to 310 °C.

Isolation and Combined Gas Chromatography–Mass Spectrometry.—Specimens of *B. xanthodes* were field-collected, reared from collected fruit or obtained from laboratory colonies. Pentane gland extracts of mature male specimens were obtained from the Vaini Research Station, Ministry of Agriculture, Tongatapu (three extracts), Koronivia Research Station, Ministry of Agriculture, Suva, Fiji (five extracts), Totokoitu Research Station, Rarotonga, Cook Islands (three extracts) and from the Ministry of Agriculture and Fisheries, Samoa (one extract). *B. krausi* specimens were obtained from a laboratory colony at the Department of Primary Industries, Indooroopilly, Queensland, which was originally cultured from infested rainforest fruit collected in North Queensland. A single *B. kirki* extract was provided from Vaini Research Station, Tonga. Three pentane gland extracts of *B. passiflorae* were obtained from a laboratory colony (Koronivia Research Station, Fiji) that was reared on a pawpaw based diet. A fourth sample was from *B. passiflorae* specimens bred from field collected rose apple (*syzygium jambos*) and fed on unrefined brown sugar and water. Two pentane gland extracts of *B. facialis* were obtained from a laboratory colony (Vaini Research Station, Tonga). This colony was reared on a pawpaw based medium. The pentane gland extracts, which were obtained from male specimens in the usual way[4] (6–25 glands per extract), were examined by capillary gas chromatography and then by GC–MS.

Compounds.—Compounds **1**–**13** and **16**–**19** are known compounds and are referenced in the text. A new, efficient synthesis of isomers of **1** is described below. An authentic sample containing **20**–**22** was kindly supplied by Dr I. Southwell. Fatty alcohol acetates were acquired by standard methods. Hexadecanyl acetate, octadecanyl acetate, *cis*-octadec-9-enyl acetate and eicosanyl acetate were prepared by acetylation of the corresponding alcohol. *cis*- and *trans*-Octadec-11-enyl acetates were prepared from the tetrahydropyranyl ether of octadec-11-ynol by standard reduction methods. *cis*-Eicos-11-enyl acetate was commercially available (Sigma Chemicals). *cis*-Eicos-13-enyl acetate was obtained by acetylation of the alcohol which resulted from $LiAlH_4$ reduction of *cis*-eicos-13-enyl acid (Sigma Chemicals). In the *B. xanthodes* extract, nonacos-9-ene had a linear retention index of 2875 (lit.,[21] 2873) and 11-, 13- and 15-methylnonacosane had 2932 (lit.,[21] 2935).

7-Methyl-1,6-dioxaspiro[4.5]decane **1**. Butyllithium (0.56 cm^3, of a 2.5 mol dm^{-3} solution in hexane, 1.41 mmol) was added to a stirred solution of acetone *N,N*-dimethylhydrazone (0.134 g, 1.34 mmol) in dry THF (tetrahydrofuran), maintained at −78 °C under a N_2 atmosphere. After 1 h, during which time a white solid formed; a THF solution (2 cm^3) of 3-tetrahydropyranyloxy-1-iodobutane (0.4 g, 1.41 mmol) was added. The initially cold solution (−78 °C) was allowed to warm to room temperature (20 °C) and then stirred overnight. The recooled solution (−78 °C) was treated with butyllithium (0.56 cm^3, 1.41 mmol) and the mixture was allowed to warm to room temperature and then stirred for 4.5 h. Ethylene oxide (0.09 g, 2.0 mmol) was added to the re-cooled mixture (−78 °C) which was allowed to warm to 20 °C and was stirred for 48 h. Dilute acid (10 cm^3 of 2 mol dm^{-3} HCl) was added and the mixture stirred for 20 min, after which it was extracted with ethyl acetate (3 × 10 cm^3). The combined organic layers were washed with brine (2 × 10 cm^3), separated, dried ($MgSO_4$) and concentrated under reduced pressure to yield a brown oil. Purification by preparative gas chromatography provided 120 mg (57%) of a mixture of racemic **2** (94%) and **3** (6%) for chiral gas chromatographic comparisons. Compound **2** exhibited ^{1}H and ^{13}C NMR spectra and low resolution MS behaviour identical with those reported.* The mass spectrum of minor component **3** was very similar to that of **2** as previously reported.[11]

(5R,7R)-7-Methyl-1,6-dioxaspiro[4.5]decane **2**. The above procedure was repeated except that (*R*)-3-tetrahydropyranyloxy-1-iodobutane **4** was utilised in the procedure. The product had concordant spectroscopic properties and exhibited $[\alpha]_D^{30} = +84.0$ (*c*, 2.2, pentane). Chiral gas chromatographic analysis (Lipodex A) showed an ee for **2** of at least 98%. This rotation may be compared with that recently reported[15] for a sample of **2** synthesised by a chemico-enzymatic approach, and shown to possess an ee of 97% $[\alpha]_D^{22} = +87.8$ (neat).

2-Hydroxyundecan-6-one **14** *and 2-Methyl-6-pentyl-3,4-dihydro-2H-pyran* **13**. Butyllithium (2.11 cm^3 of a 2.5 mol dm^{-3} solution in hexane, 5.28 mmol) was added to a stirred solution of acetone *N,N* dimethylhydrazone (0.528 g, 5.28 mmol) in dry THF, maintained at −78 °C under a N_2 atmosphere. After 1 h, during which time a white solid formed, a THF solution (5 cm^3) of 3-tetrahydropyranyloxy-1-iodobutane (1.00 g, 3.52 mmol) was added. The initially cold solution (−78 °C) was allowed to warm to room temperature (20 °C) and then stirred overnight. The residue obtained after removal of THF was taken up in ether–pentane (1:1) and filtered through a pad of neutral alumina (activity I), dried (Na_2SO_4), and concentrated to yield the crude monoalkylated hydrazone (0.611 g, 2.39 mmol, 68%). This crude product in dry THF (7 cm^3) was added dropwise to a stirred solution of LDA (3.82 mmol) in THF (15 cm^3) maintained at −78 °C under N_2. After stirring for 45 min, butyl bromide (0.392 g, 2.86 mmol) in dry THF (5 cm^3) was added dropwise, and stirring was continued for a further 20 min at −78 °C, and then overnight at room temperature. Dilute acid (5 cm^3 of 10% HCl) was added and the mixture stirred for 30 min, after which time it was extracted with ether (3 × 30 cm^3). The combined organic layers were washed with saturated $NaHCO_3$ solution (2 × 30 cm^3), dried ($MgSO_4$) and concentrated under reduced pressure to yield a yellow oil. The keto alcohol **14** and hemiketal **15** were obtained as a mixture (*ca.* 5:1) by preparative HPLC, using 20:80 ethyl acetate–hexane; $\delta_H(C_6D_6)$ 0.84 (t, J 7.3, 3 H, CH_2CH_3 of **14**), 0.87 (t, J 7.08, CH_2CH_3 of **15**), 1.00 [d, J 6.11, 3 H, CH(OH)CH_3 of **14**], 1.10–

* For a summary of synthesis and spectroscopic data see refs. 15 and 35.

1.64 (m), 1.97 [t, *J* 7.08, 2 H, C(O)CH_2 of **14**], 1.98 [t, *J* 7.08, 2 H, C(O)CH_2 of **14**], 3.50 [sextet, *J* 6.11, 1 H, C*H*(OH) of **14**] and 3.98 [m, C*H*(OH) of **15**]; $\delta_C(C_6D_6)$ **14**: 14.09, 20.13, 22.80, 23.75 (2 C), 31.72, 39.01, 42.40, 42.55, 67.25 and 209.23; **15** 14.23, 19.59, 22.36, 23.01, 23.17, 32.54, 32.84, 33.36, 43.98, 65.97 and 96.76; GC–MS analysis of the mixture of **14** and **15** showed only **14** and the dehydration product **13**,[27] with **15** presumably dehydrating to **13** under the chromatography conditions; *m/z* **14** 186 (M^+, 0%), 168 (3), 125 (7); 112 (25), 99 (42), 97 (43), 83 (13), 73 (12), 71 (45), 69 (41), 58 (22), 55 (50), 45 (19) and 43 (100).

Preparative gas chromatography (Carbowax C20W) of the mixture of **14** and **15** provided the dihydropyran **13** by cyclisation–dehydration; $\delta_H(C_6D_6)$ 0.86 (t, *J* 7.08, 3 H), 1.15 (d, *J* 6.11, 3 H) 1.25–1.48 (m, 6 H), 1.56–1.63 (m, 2 H), 1.80–2.00 (m, 2 H), 2.12 (t, *J* 7.45, 2 H), 3.78 (dqd, *J* 9.76, 6.35, 2.44, 1 H) and 4.50 (m, 1 H); $\delta_C(C_6D_6)$ 14.22, 20.85, 21.24, 22.88, 27.28, 29.62, 31.79, 34.86, 71.48, 94.35 and 154.90; *m/z* **13** 168 (M^+, 14%), 125 (31), 112 (79), 97 (28), 84 (25), 83 (33), 71 (10), 70 (34), 58 (21), 57 (17), 55 (100) and 43 (75) (Found: M^+, 168.1539. $C_{11}H_{20}O$ requires *M*, 168.1514); $[\alpha]_D^{22} = +45.45$ (*c*, 0.885, pentane).

Acknowledgements

The authors are grateful to Dr. Allan Allwood, Koronivia Research Station, Nausori, Fiji, for obtaining *B. xanthodes* and *B. passiflorae* gland extracts, to Ms Marlene Elson-Harris and Mr. Eddie Hamacek, Department of Primary Industries, Indooroopilly, Queensland, for obtaining specimens and gland extracts, and to Dr. Joseph Brophy, Department of Chemistry, University of New South Wales for long chain hydrocarbon mass spectra. Dr. Ian Southwell of the Wollongbar Agricultural Institute, Wollongbar, New South Wales, Australia, kindly made available a sample containing *cis*- and *trans*-sabinene hydrates (thujan-4-ols) and terpinen-4-ol.

References

1 See, for example, *Fruit-Flies*, ed. A. P. Economopoulous; Proceedings second Int. Symp. Colymbari, Crete, September, 1986, Elsevier Science Publishers, Amsterdam, 1987. ISBN: 0-444-98946-3.
2 R. Baker, R. Herbert, P. E. House, O. T. Jones, W. Francke and W. Reith, *J. Chem. Soc., Chem. Commun.*, 1980, 52.
3 R. Baker and R. H. Herbert, *J. Chem. Soc., Perkin Trans. 1*, 1987, 1123.
4 W. Kitching, J. A. Lewis, M. V. Perkins, R. A. I. Drew, C. J. Moore, V. Schurig, W. A. König and W. Francke, *J. Org. Chem.*, 1989, **54**, 3893.
5 M. V. Perkins, W. Kitching, R. A. I. Drew, C. J. Moore and W. A. König, *J. Chem. Soc., Perkin Trans. 1*, 1990, 1111.
6 S. Krohn, M. T. Fletcher, W. Kitching, R. A. I. Drew, C. J. Moore and W. Francke, *J. Chem. Ecol.*, 1991, **17**, 485.
7 G. Haniotakis, W. Francke, K. Mori, H. Redlich and V. Schurig, *J. Chem. Ecol.*, 1986, **12**, 11.
8 T. E. Bellas and B. E. Fletcher, *J. Chem. Ecol.*, 1979, **5**, 795.
9 R. A. I. Drew, *Tropical Fruit-Flies of the Australasian and Oceanian Regions, Mem. Qld. Mus.*, 1989, **26**, 1–521. Brisbane ISSN 0079-8835.
10 J. H. Tumlinson, *Pure Appl. Chem.*, 1989, **61**, 559.
11 (*a*) W. Francke and W. Reith, *Liebigs Ann. Chem.*, 1979, 1; (*b*) W. Francke, G. Hindorf and W. Reith, *Naturwissenschaften*, 1979, **66**, 619.
12 (*a*) E. J. Corey and D. Enders, *Tetrahedron Lett.*, 1976, 3; (*b*) D. Enders in *Current Trends in Organic Synthesis*, ed. H. Nozaki, Pergamon Press, Oxford, UK, 1983, 151.
13 K. Mori and H. Watanabe, *Tetrahedron*, 1986, **42**, 295.
14 M. V. Perkins, M. F. Jacobs, W. Kitching, P. J. Cassidy, J. A. Lewis and R. A. I. Drew, *J. Org. Chem.*, 1992, **57**, 3365.
15 S. Ramaswamy and A. C. Oehlschlager, *Tetrahedron*, 1991, **47**, 1157.
16 K. Hintzer, R. Weber and V. Schurig, *Tetrahedron Lett.*, 1981, **22**, 55.
17 R. Jacobson, R. J. Taylor, H. J. Williams and L. R. Smith, *J. Org. Chem.*, 1982, **47**, 3140.
18 W. Francke, unpublished results.
19 H. R. Buser, H. Arn, P. Guerin and S. Rauscher, *Anal. Chem.*, 1983, **55**, 818.
20 M. S. Vigdergauz and A. A. Martynov, *Chromatographia*, 1971, **4**, 463.
21 Mass spectral collection of Dr J. Brophy, University of New South Wales. See J. J. Brophy, G. W. K. Cavill, N. W. Davies, T. D. Gilbert, R. P. Philip and W. D. Plant, *Insect Biochem.*, 1983, **13**, 381.
22 W. Francke, W. Reith, G. Bergström and J. Tengö, *Naturwissenschaften*, 1980, **67**, 149.
23 M. V. Perkins, W. Kitching, W. A. König and R. A. I. Drew, *J. Chem. Soc., Perkin Trans. 1*, 1990, 2501.
24 W. Kitching, J. A. Lewis, M. T. Fletcher, R. A. I. Drew, C. J. Moore and W. Francke, *J. Chem. Soc., Chem. Commun.*, 1986, 853.
25 W. Francke, W. Reith and V. Sinwell, *Chem. Ber.*, 1980, **113**, 2686.
26 (*a*) M. V. Perkins, M. T. Fletcher, W. Kitching, R. A. I. Drew and C. J. Moore, *J. Chem. Ecol.*, 1990, **16**, 2475; (*b*) M. G. O'Shea and W. Kitching, *Tetrahedron*, 1989, **45**, 1177.
27 W. Francke, W. Mackrenroth, W. Schröder, S. Schulz, J. Tengö, E. Engels, W. Engels, R. Kittmann and D. Schneider, *Z. Naturforsch., C*, 1985, **40**, 145.
28 (*a*) T. E. Bellas and B. S. Fletcher, *J. Chem. Ecol.*, 1979, **5**, 795; (*b*) R. Baker, R. H. Herbert and R. A. Lomer, *Experientia*, 1982, **38**, 232; (*c*) J. A. Lewis, Ph.D. Thesis, The University of Queensland, 1987.
29 G. Vernin, G. Vernin, J. Metzger, C. Rogue and J.-C. Pieribattesti, *J. Ess. Oil Res.*, 1991, **3**, 83.
30 J. Heidlas, M. Lehr, H. Idstein and P. Schreier, *J. Agric. Food Chem.*, 1984, **32**, 1020.
31 (*a*) R. Baker, R. H. Herbert and G. G. Grant, *J. Chem. Soc., Chem. Commun.*, 1985, 824; (*b*) Unpublished results (The University of Queensland) of J. J. De Voss, S. Krohn and M. T. Fletcher.
32 W. Francke and J. P. Vité, *Z. Angew. Entomol.*, 1983, **96**, 146.
33 U. Kohnle, W. Francke and A. Bakke, *Z. Angew. Entomol.*, 1985, **100**, 5.
34 C. Chararas, J. Riviere, C. Ducauze, D. Rutledge, G. Delpui and M.-T. Cazelles, *C. R. Acad. Sci. Paris, Ser. D.*, 1980, **291**, 299.
35 G. Rosini, R. Ballini and E. Marotta, *Tetrahedron*, 1989, **45**, 5935 and refs. therein.

Paper 2/03692D
Received 13*th July* 1992
Accepted 29*th July* 1992