Letters to the Editor

One-step transformation of sulfonyl chlorides into β-substituted acroleins

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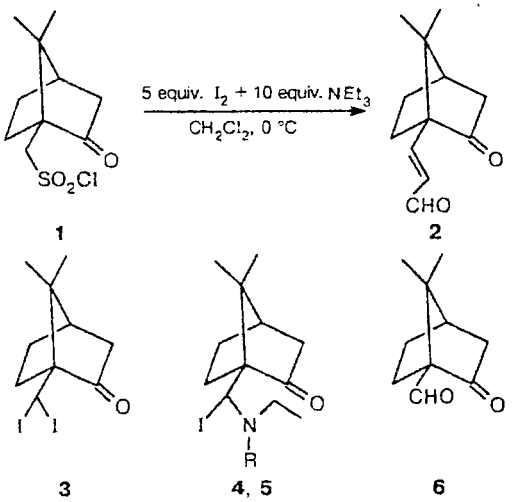
We have found that the reaction of (+)-10-camphorsulfonylchloride (**1**) with I_2NEt_3 in CH_2Cl_2 at 0 °C affords α,β-unsaturated aldehyde (**2**) in 50% yield. *gem*-Diiodo-derivative (**3**) (~16%) and iodoaminals (**4**) and (**5**) (~7%) are minor products in this reaction. The structure of aldehyde **2** is confirmed by spectral data and chemical transformations. In particular, oxidative cleavage of the double bond in **2** with an OsO_4(cat.)—$NaIO_4$[1] system results in the known oxoaldehyde (**6**).[2,3] Studies of the mechanism and synthetic potential of this new reaction are now in progress in our laboratory.



(1*S*,4*R*)-1-[(*E*)-2-(Formyl)vinyl]-7,7-dimethylbicyclo[2.2.1]heptan-2-one (2). $[\alpha]_D^{20}$ +6.2° (*c* 1.0, $CHCl_3$). M.p. 77—78 °C. ^1H NMR ($CDCl_3$), δ: 1.00 (s, 6 H, 6-H_{endo}); 1.65 (dd, 1 H, 5-H_{endo}, J = −9.9 and 5.6 Hz); 2.00 (d, 1 H, 3-H_{exo}, J = −18.4 Hz); 2.12 (m, 2 H, 5-H_{exo}, 6-H_{exo}); 2.52 (ddd, 1 H, 3-H_{endo}, J = −18.4, 2.3, and 4.7 Hz); 6.3 (dd, 1 H, 2′-H, J = 7.8 and 16.3 Hz); 6.85 (d, 1 H, 1′-H, J = 16.3 Hz). ^{13}C NMR ($CDCl_3$), δ: 19.56 (CH_3); 20.20 (CH_3); 27.01 (C(5)) and 27.10 (C(6)); 43.56 (C(3)); 43.89 (C(4)); 50.29 (C(7)); 64.18 (C(1)); 135.61 (C(2)); 151.88 (C(1′)); 193.55 (CHO); 214.47 (C(2)). MS, *m/z* (I_{rel} (%)): 192 $[M]^+$ (28), 177 $[M-CH_3]^+$ (11), 175 $[M-OH]^+$ (20); 174 $[M-H_2O]^+$ (30), 164 $[M-CO, M-C_2H_4]^+$ (100), 159 $[M-CH_3-H_2O]^+$ (8), 149 $[M-CH_2=C-OH]^+$ (84).

(1*S*,4*R*)-1,1-Diiodomethyl-7,7-dimethylbicyclo[2.2.1]heptan-2-one (3). $[\alpha]_D^{20}$ +28.9° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$), δ: 1.20 (s, 3 H, CH_3); 1.21 (s, 3 H, CH_3); 1.38 (m, 1 H, 5-H_{endo}); 1.90 (m, 1 H, 6-H_{endo},); 1.95—2.10 (m, 3 H, 6-H_{exo}, 5-H_{exo}, 4-H); 2.09 (d, 1 H, 3-H_{exo}, J = −18.5 Hz); 2.54 (ddd, 1 H, 3-H_{endo}, J = 3.9, 5.0, and 18.5 Hz); 5.26 (s, 1 H, CHI_2). ^{13}C NMR ($CDCl_3$), δ: −37.97 (CHI_2); 21.87 (CH_3); 23.37 (CH_3); 25.57 (C(5)); 33.12 (C(6)); 43.01 (C(3)); 46.25 (C(4)); 50.02 (C(7)); 62.70 (C(1)); 211.28 (C(2)). Found (%): C, 30.01; H, 3.6; I, 60.07. $C_{10}H_{24}I_2O$. Calculated (%): C, 29.70; H, 3.50; I, 62.80.

(1*S*,4*R*)-[(1-Ethylamino-1-iodo)methyl]-7,7-dimethylbicyclo[2.2.1]heptan-2-one (4). $[\alpha]_D^{20}$ +67.5° (*c* 1.0, $CHCl_3$). ^1H NMR ($CDCl_3$), δ: 1.20—1.30 (m, 1 H); 1.23 (s, 3 H, CH_3); 1.25 (t, 3 H, CH_3, J = 7.1 Hz); 1.34 (s, 3 H, CH_3); 1.60 (ddd, 1 H, 5-H_{endo}, J = −9.3, 4.3, and 8.8 Hz); 2.00 (d, 1 H, 3-H_{endo}, J = −18.5 Hz); 2.05 (m, 2 H, 4-H, 6-H_{exo}); 2.52 (ddd, 1 H, 3-H_{exo}, J = −18.5, 3.9 and 4.2); 2.99 (ddd, 1 H,

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6-H_{endo}, J = −9.3, 4.5, and 8.8 Hz); 3.30 (sext, 2 H, NCH_2, J = 7.1 Hz); 3.60 (br.s, NH); 5.34 (s, 1 H, CHI). ^{13}C NMR ($CDCl_3$), δ: 14.51 (CH_3); 21.65 (CH_3); 22.81 (CH_3); 25.94 (C(5)); 29.03 (C(6)); 38.16 (I—C—N); 42.78 (C(3)); 43.56 (C—N); 45.70 (C(4)); 49.37 (C(7)); 63.12 (C(1)); 213.69 (C(2)). Found (%): C, 44.50; H, 5.95; I, 38.62, N, 4.10. $C_{12}H_{20}INO$. Calculated (%): C, 44.90; H, 6.20; I, 39.50, N, 4.40.

References

1. R. Rappo, D. S. Allen, R. U. Lemieux, and W. S. Johnson, *J. Org. Chem.*, 1956, **21**, 478.
2. T. Polonski, *J. Chem. Soc., Perkin Trans. 1*, 1983, 305.
3. L. A. Paquette, S. C. Huber, and R. S. Thompson, *J. Org. Chem.*, 1993, **58**, 6874.

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Cyclic sesquiterpenes in the volatile secretions of potato leaves (*Solanum tuberosum* L.) and Colorado beetle (*Leptinotarsa decemlineata* Say)

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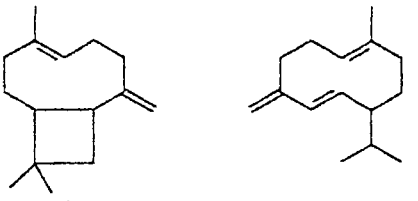
Volatile secretions of potato leaves are an important factor for the attraction of Colorado beetles *Leptinotarsa decemlineata* Say.[1] More than 50 compounds have been identified among the scents of the plants of the *Solanum* family and the electrophysiological reaction of Colorado beetle for these compounds has been studied.[2] However, none of these compounds exhibited attractant properties with respect to Colorado beetle in olfactometric tests.[3]

We carried out chromatomass-spectrometric studies (GC/MS) of volatile organic substances of potato *Solanum tuberosum* L. and identified the sesquiterpene caryophyllene (**1**) that has not been found previously.[4] The molecular ion with m/z 204 corresponds to the compound **1**. Its mass spectrum (MS) contains also the characteristic ion with m/z 189, which is due to the elimination of one of the methyl groups of the cyclobutane fragment of compound **1**. In addition, ions with m/z 133, 93, and 69 typical of the MS of sesquiterpene **1**[5] are also observed. The correctness of the assignment is confirmed by the coincidence of the retention times of the isolated compound and the authentic sample of **1**.

The results of the GC/MS study of the volatile secretions of Colorado beetle imago appeared to be rather illustrative. Two compounds with identical molecular weights of 204 corresponding to the molecular formula $C_{15}H_{24}$ and in the ratio 10 : 1 were found in the samples independent of the insect sex. The main component was identical with caryophyllene **1**, whereas according to the mass spetrum, the minor one corresponds to germacrene-D (**2**).[6] The ion with m/z 161 typical of compound **2** corresponding to the elimination of the isopropyl group from the $[M]^+$ ion and the ions with m/z 119, 105, 91, and 77 indicating the formation of alkylaromatic structures should be especially noted.



1 **2**

The detection of compound **1** in the volatile secretions of potato and Colorado beetle may indicate the role of this sesquiterpene as food attractant for this insect. In fact, our olfactometric observations confirmed the existence of attractant properties of compound **1** with respect to Colorado beetle. Moreover, a linear dependence between the attracting effect for Colorado beetle and the content of caryophyllene **1** in volatile secretions of different potato species was found.

References

1. D. Thiery and J. H. Visser, *Entomol. Exp. et Appl.*, 1986, **41**, 165.
2. J. H. Visser, *Entomol. Exp. et Appl.*, 1979, **25**, 86.
3. J. H. Visser and D. A. Ave, *Entomol. Exp. et Appl.*, 1978, **24**, 538.
4. D. Thiery and J. H. Visser, *Sciences de la Vie*, 1995, **318**, 105.
5. W. H. McFadden and R. G. Buttery, in *Topics in Organic Mass Spectrometry*, Ed. A. L. Burlingame, Wiley-Interscience, New York, 1970, **8**, 327.
6. G. R. Waller, *Biochemical Application in Spectrometry*, Wiley-Interscience, New York, 1980, 1279 pp.

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