The principal axes of the 50%-thermal vibration ellipsoids for C- and O-atoms vary between 0.18 and 0.35 Å. A qualitative impression of the relative orientation of the ellipsoids can be obtained from the stereoscopic drawing of the molecule in Fig. 3[2]), which also shows the overall conformation of the steroid. The A-ring has a 'twist'-conformation with an approximate twofold-axis through the middle of the 4,5-double bond and C(1)–C(2). The B-ring has a chair conformation slightly distorted due to the $sp^2$-character of C(5); the C-ring is an almost undistorted chair conformation, with torsion angles slightly less than the ideal 60°, $\langle|\tau|\rangle = 56°$, and the five-membered D-ring is in an envelope conformation with C(13) as flap (for torsion angles see Fig. 2). The $\beta$-acetyl substituent at C(17) has the keto group almost *syn*-planar with C(16)–C(17), which brings O(23) to a distance of about 2.4 Å from the $\beta$-hydrogen on C(16). A calculation of all intra- and intermolecular distances revealed no abnormally close contacts. A packing diagram is shown in Fig. 4.

The authors express sincere thanks to Dr. *R. V. Coombs* and co-workers at *Sandoz-Wander Inc.*, Hanover, N.J., who prepared the rac-$\psi$-retroprogesterone by total synthesis.

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[2]) This drawing has been calculated with the program ORTEP (*C. K. Johnson*, Oak Ridge (1965)), adapted to an U-1108 Computer, plotted on a *Benson-Lehner* Plotter.

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## 19. A Chemical Study of *Burley* Tobacco Flavour (*Nicotiana tabacum* L.) IV. Identification of Seven New Solanone Metabolites Including 7,8-Dioxabicyclo[3.2.1.]octane- and 4,9-Dioxabicyclo[3.3.1]nonane Derivatives[1])

Preliminary Communication

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(28. XI. 73)

To date, our continuing study of *Burley tobacco condensate*[2]) has already lead to the isolation and identification of more than 300 constituents of this flavour [1], including new chemical entities such as *solanofuran* and *spiroxabovolide* [1c]. Investi-

[1]) For the 3rd publication of this series see [1c].
[2]) *Burley* tobacco condensate and fractions B1, B2 and B3 were prepared as previously described [1a–b].

gation of a number of other novel constituents is in progress or has just been completed, as is the case for the following seven compounds.

1. *(1-Methyl-4-isopropyl-7,8-dioxabicyclo[3.2.1]octan-6-yl) methyl ketone* (**1**) was isolated from subfractions B2-PN-f and B3-PN-d[3]. – MS.[4] (*m/e* (% relative abundance)): 43 (100), 55 (11.5), 71 (8.5), 81 (13), 99 (20), 109 (8.5), 169 (38), very weak parent peak ($M^+ = 212$). This compound was identified by direct comparison with an authentic sample prepared by acid-catalyzed isomerisation of 3,4-epoxy-5-isopropylnonane-2,8-dione (**6**)[5]).

2. *1-(1-Methyl-4-isopropyl-7,8-dioxabicyclo[3.2.1]octan-6-yl)-ethanol* (**2**) was found to occur in subfraction B2-PN-i. – MS.: 43 (100), 55 (14), 69 (11), 82 (22), 99 (17.5), 111 (16.5), 129 (33), 169 (34.5), 171 (13.5), no discernible parent peak ($M^+ = 214$). This compound resulted from $NaBH_4$ reduction of **1**[5]).

3. *2-(1-Methyl-4-isopropyl-7,8-dioxabicyclo[3.2.1]octan-6-yl)-propan-2-ol* (**3**) occurred in subfractions B2-PN-h and B3-PN-h. – MS.: 43 (100), 59 (51), 71 (13.5), 82 (30), 97 (52.5), 112 (8), 125 (6), 140 (31.5), 169 (32), no discernible parent peak ($M^+ = 228$). This compound was synthesized, together with **4**, by acid-catalyzed isomerisation of 5-isopropyl-6,7-epoxy-8-hydroxy-8-methylnonan-2-one (**5**)[5]).

4. *3,3,5-Trimethyl-8-isopropyl-4,9-dioxabicyclo[3.3.1]nonan-2-ol* (**4**) was isolated from subfraction B3-PN-h. MS.: 43 (100), 55 (14), 70 (21), 81 (32.5), 97 (15.5), 112 (57), 127 (12), 170 (11), 185 ($< 1$), no discernible parent peak ($M^+ = 228$). This compound was synthesized, together with **3**, by acid-catalyzed isomerisation of 5-isopropyl-6,7-epoxy-8-hydroxy-8-methylnonan-2-one (**5**)[5]).

5. *5-Isopropyl-6,7-epoxy-8-hydroxy-8-methylnonan-2-one* (**5**) was identified in subfraction B3-PN-i. – MS.: 43 (100), 59 (30), 69 (18.5), 81 (20), 97 (23), 112 (18), 123 (2.5), 139 (3), 169 ($< 1$), no discernible parent peak ($M^+ = 228$). This compound was synthesized by direct epoxidation of 'solanone hydrate' **7**[5]).

6. *3,4-Epoxy-5-isopropylnonane-2,8-dione* (**6**) was isolated from subfractions B3-PN-g and -h (2 stereoisomers). – MS. of the *cis* isomer: 43 (100), 55 (10), 71 (5), 85 (14.5), 93 (5), 109 (9), 123 (3.5), 151 (2), 169 (7), no discernible parent peak ($M^+ = 212$). *Trans* isomer: 43 (100), 55 (11), 71 (5), 85 (18.5), 97 (4.5), 109 (4), 123 (3.5), 151 ($< 1$), 169 ($< 1$), no discernible parent peak. The latter stereoisomer (as a mixture of two diastereoisomers) was synthesized from *norsolanadione* **8**[5]).

7. trans-*5-Isopropyl-8-hydroxy-8-methylnon-6-en-2-one* (**7**) or 'solanone hydrate' was identified in subfractions B2-PN-i and B3-PN-i. – MS.: 43 (100), 55 (8), 69 (15), 81 (7.5), 93 (34), 109 (13), 121 (22), 136 (17), 151 (2), 194 (6.5), no discernible parent peak ($M^+ = 212$). This compound was also synthesized from *norsolanadione* **8**[5]).

Compounds **1**, **3** and **4** are possibly formed in tobacco by direct isomerisation of the solanone-related precursors **5** and **6**, *i.e.* through the same process we used to synthesize them. Such reactions are well-documented. For instance, studies conducted in the *manool* [2], *brevicomin* [3] and *1-acetoxy-3,4-epoxypentane* [4] series clearly demonstrate that $\delta$, $\varepsilon$-epoxycarbonyl compounds like **5** and **6** are easily and stereospecifically isomerised to internal acetals on heating, or by acid treatment.

The stereochemistry of tobacco acetals **1–4** will be discussed in our full report on the present work.

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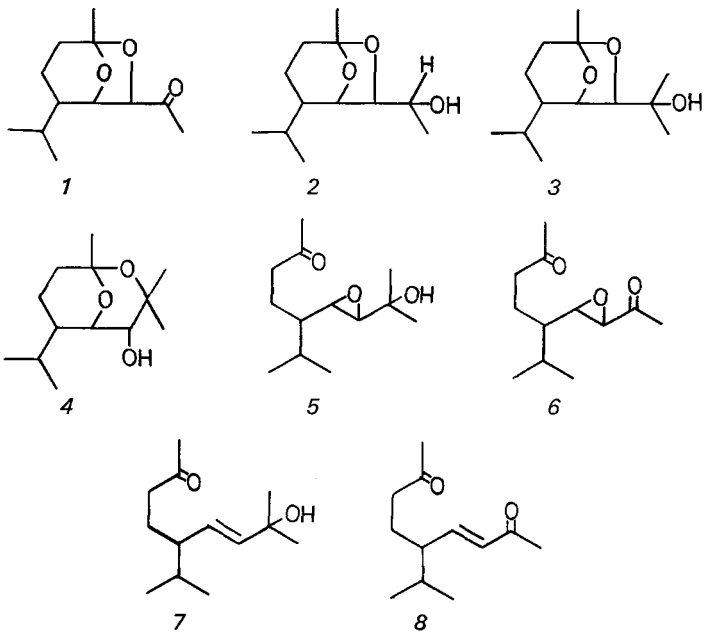
[3]) Subfractions B2-PN-a to -j were obtained and investigated as previously described [1a]. The preparation of subfractions B3-PN-a to -i and their study will be the subject-matter of a future paper.

[4]) Mass spectra were measured on the *Atlas* CH 4 mass spectrometer at 70 eV (inlet temperature ~150°).

[5]) Our synthetic work will be described in the full paper.



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## 20. Synthesis and Ring Opening of 1,4-Dicyanobicyclo[2.2.0]hexane. Radical Stabilization Energy of a Cyano Group[1])

Preliminary Communication

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(22. XII. 73)

*Summary.* 1,4-Dicyanobicyclo[2.2.0]hexane (**2**) was prepared by (2+2)-photocycloaddition of ethylene to 1,2-dicyanocyclobutene. **2** isomerizes cleanly to 2,5-dicyanohexadiene-1,5 (**3**) with a very low activation energy of 21.7 ± 1.4 kcal/mol. From comparison with the reported rates of isomerization of bicyclo[2.2.0]hexane, the radical stabilization energy of the cyano group is shown to be about 7.3 kcal/mol.

[1]) Synthesis and Reactivity of Compounds with Cyclobutane Ring(-s). Part IV. For Part III see [1].