DICAMPHORYLMETHANE – A NEW CAMPHOR DERIVATIVE

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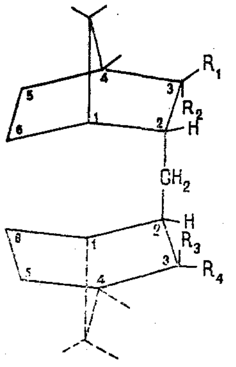
It is known that under the action of bases camphor is converted into a dimer – dicamphor [1]. On treating camphor with NaH or LiH in dimethylformamide (DMFA) we obtained a compound differing from dicamphor. Thus, for example, by heating a mixture of 0.5 g of d-camphor and 0.08 g of NaH (or 0.1 g of LiH) in 4 ml of absolute DMFA at 50°C for 10 min and at 90°C for 10 min followed by dilution with 5% hydrochloric acid and extraction with ether, we obtained a compound not described previously consisting of bis-(3-oxo-4,7,7-trimethyl-bicyclo[2,2,1]hept-2-yl)methane (dicamphorylmethane) (I): $C_{21}H_{32}O_2$, mp 195-196°C (from hexane), $[\alpha]_D^{20}$ +69.79° (c 6.2; ethanol); IR spectrum, λ_{max} cm^{-1}: 1380, 1398 (C–CH$_3$), 1750 (O=C$\langle$). PMR spectrum, 0.88, 0.90, 0.97 (s, 6 CH$_3$). Mass spectrum, m/z: 316 (100%, M$^+$), 301, 288 (100%), 273, 165, 152 (100%) m/z. At the melting point, compound (I) decomposed with the formation of camphor, and on heating with D_2O in an alkaline medium two hydrogen atoms were replaced by deuterium. The reduction of (I) with $LiAlH_4$ in ether gave two isomeric diols $C_{21}H_{34}O_2$ (II and III). Compound (II) had mp 198-200°C. IR spectrum, λ_{max}^{KBr}, cm^{-1}: 3400 (–OH). PMR spectrum, ppm: 3.02 (d, J = 3.0 Hz, 2 $\mathrm{H-\overset{|}{\underset{|}{C}}-O}$). Mass spectrum, m/z: 302 (M$^+$ – 18). Diacetate (IV): $C_{25}H_{38}O_4$. PMR spectrum, ppm: 4.22 (d, 2 $\mathrm{H-\overset{|}{\underset{|}{C}}-OAc}$). Compound (III) had mp 203-205°C. IR spectrum, λ_{max}^{KBr}, cm^{-1}; 3430 (–OH). PMR spectrum, ppm: 3.0 (d, J = 3.5 Hz, 1 $\mathrm{H-\overset{|}{\underset{|}{C}}-O}$) 3.85 (d, J = 10.0 Hz, 1 $\mathrm{H-\overset{|}{\underset{|}{C}}-O}$). Mass spectrum, m/z: 302 (M$^+$ – 18). Diacetate (V): $C_{25}H_{38}O_4$. PMR spectrum, ppm: 4.18, 4.86 (2d, 2 $\mathrm{H-\overset{|}{\underset{|}{C}}-OAc}$)

On comparing the values of the chemical shifts obtained with those described for the protons of bicyclo-[2,2,1]heptane [2], it was concluded that in (II) the protons at C_3 were endo-oriented (exo-OH group), and in (III) one H was in the endo orientation and the other in the exo orientation (exo- and endo-OH groups, respectively). The spin–spin coupling constants of the H_3 protons of the compound (II) (J = 3.0 Hz) show the mutual trans arrangement of the H_2 and H_3 protons. In compound (III), one of the H_3 protons is located relative to the H_2 in the trans position (J = 3.5 Hz) and the other in the cis position (J = 10.0 Hz). According to the facts given above, in both compounds the CH_2 group is located in the most stable endo position with respect to both bicyclic systems, and, consequently, the structure and stereochemistry of the initial compound are expressed by formula (I).



I. $R_1 + R_2 = R_3 + R_4 = O$
II. $R_1 = R_4 = OH$; $R_2 = R_3 = H$
III. $R_1 = R_3 = OH$; $R_2 = R_4 = H$
IV. $R_1 = R_4 = OAc$; $R_2 = R_3 = H$
V. $R_1 = R_3 = OAc$; $R_2 = R_4 = H$

Thus, compound (I) is the product of the condensation of two molecules of camphor with formaldehyde, the source of which was the dimethylformamide.

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IR spectra were taken on a Specord-75 instrument in CCl_4 and PMR spectra on a Tesla BS-467 instrument (with a working frequency of 60 MHz; internal standard TMS; CCl_4; δ scale). Mass spectra were obtained on a MKh-1302 instrument. The analyses of all the compounds corresponded to the calculated figures.

LITERATURE CITED

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AJAFIN — A NEW GUAIANOLIDE FROM *Ajania fastigiata*

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Continuing an investigation of the lactones of the epigeal part of *Ajania fastigiata* (c. Winkl), Poljak. [1, 2], we have chromatographed a benzene extract of chloroform-extracted material [3] on a column of silica gel (type KSK). From the fractions eluted by benzene–acetone (10 : 1) we have isolated a lactone with mp 212-213°C (benzene–acetone). The lactone proved not to have been described in the literature and has been called ajafin (I). Ajafin has the composition $C_{16}H_{20}O_6$, M^+ 308, $[\alpha]_D^{22}$ +34.7° (c 3.57 methanol). The IR spectrum of (I) (tablets with KBr) contains absorption bands at (cm^{-1}) 3410-3440 (OH), 1740-1750 (C=O of a γ-lactone and of a cyclopentanone), and 1659 (C=C) [4]. The PMR spectra of (I) (deuteropyridine, 0 — HMDS) shows signals at the following δ values (ppm): 1.53 (3 H, br. s, $CH_3-C=C$); 1.72 (3 H, s, CH_3-C-O); 3.15 (3 H, s, CH_3-O-); 3.85 (2 H, m, H-2 and H-6); and 6.26 and 6.51 (1 H each, Tr, $=CH_2$). The H-2 signal appears in the form of a singlet and is superposed on the central component of the triplet from H-6.

The values of the chemical shifts of the protons of the exomethylene group show the presence of a hydroxy group in the β position, i.e., at C-8 [5]. The hydrogenation of (I) with $NaBH_4$ gave dihydroajafin (II), $C_{16}H_{22}O_6$, M^+ 310, mp 223-225°C. The IR spectra of (II) showed absorption bands at (cm^{-1}) 1770 (C=O, carbonyl of a γ-lactone), 1750 (C=O of a cyclopentanone), and 1670 (C=C). The IR spectra of (I) and (II), and also the PMR spectrum of (I) permit ajafin to be assigned to the guaianolides. The PMR spectrum of (II), unlike that of (I), shows the signal of a methyl group at a secondary carbon atom in the form of a doublet at 1.55 ppm (3 H, J = 7 Hz; CH_2-CH_3).

The hydrogenation of (II) in the presence of PtO_2 in ethanol gave tetrahydroajafin (III). The acetylation of (III) with acetic anhydride in pyridine led to diacetyltetrahydroajafin (IV), $C_{20}H_{26}O_8$, mp 145-146°C (hexane–acetone); M^+ 396, the IR spectrum of which exhibited absorption bands at (cm^{-1}) 1787 (C=O of a γ-lactone), 1740 (C=O of a cyclopentanone), and 1730 and 1242 ($OCOCH_3$). The PMR spectrum of (IV) contained signals at the following δ values (ppm): 1.28 (3 H, d, J = 7 Hz, $C_{11}-CH_3$); 1.40 (3 H, s, C_4-CH_3; 3 H, br. s, $C_{10}-CH_3$); two singlets at 1.88 and 1.93 (3 H, $OCOCH_3$, each) 3.07 (3 H, s, OCH_3); 4.20 (1 H, tr, Σ^3J = 20 Hz, H-6); 4.85 (1 H, d. tr. ^3J = 9.5, 9.5, and 4.2 Hz, H-8); 5.27 (1 H, d, J = 4.0 Hz, H-2).

The doublet splitting of the signal at 5.27 ppm and its spin–spin coupling constant (J = 4.0 Hz) show that one of the acetyl groups in (IV) is present in the cyclopentane ring at C-2, and the carbonyl group is at C-3. The absence of the signal of an olefinic proton and the triplet nature of the lactone proton indicate the position of the endocyclic double bond at C_1-C_{10}.

According to the information given, ajafin has the structure of 2,8-dihydroxy-4-methoxy-3-oxo-5,7α(H)-6,8β(H)-guaia-1(10),11(13)-dien-6,12-olide (I).

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