LITERATURE CITED

1. E. G. Bobrov, Forest-Froming Conifers of the USSR [in Russian], Nauka, Leningrad (1978).
2. T. Norlin and B. Winell, Acta Chem. Scand., 26, 2289 (1972).
3. J. P. Kuthey, I. H. Rogers, and J. W. Rowe, Tetrahedron, 25, 3731 (1969).
4. N. A. Vasil'eva and I. S. Geles, The Chemistry and Use of the Extractive Substances of Trees: Abstracts of Lectures at the IIIrd All-Union Scientific and Technical Conference [in Russian], Gor'kii (1990), p. 98.
5. M. L. Laver and H. H. L. Fang, J. Agric. Food Chem., 37, 114 (1989).
6. . . Kolattukudy, Chemistry and Biochemistry of Natural Waxes, Elsevier, Amsterdam (1976), p. 247.
7. V. A. Pentegova, Zh. V. Dubovenko, V. A. Raldugin, and É. N. Schmidt, The Terpenoids of Doniferous Plants [in Russian], Nauka, Novosibirsk (1987), p. 71.
8. J. W. Rowe, Phytochemistry, 4, 1 (1965).
9. T. W. Norin and B. Winell, Acta, Chem. Scand., 26, 2297 (1972).
10. N. V. Kovganko and Zh. N. Kashkan, Khim. Prir. Soedin., No. 6, 771 (1990).
11. D. H. R. Barton and K. H. Overton, J. Chem. Soc., 2639 (1955).
12. Y. Tsuda, T. Sano, K. Kawaguchi, and Y. Inubushi, Tetrahedron Lett., 1279 (1964).
13. T. Norin, Phytochemistry, 11, 1231 (1972).
14. R. M. Carman and H. C. Deeth, Aust. J. Chem., 24, 1099 (1971).
15. J. de Pascual Teresa, A. F. Barrero, L. Muriel, A. San Feliciano, and M. Grande, Phytochemistry, 19, 1153 (1980).
16. G. F. Chernenko, E. E. Ivanova, L. I. Demenkova, and É. N. Shmidt, Khim. Prir. Soedin., No. 5, 645 (1990).
17. X. A. Dominguez and V. Barragan, J. Org. Chem., 30, 2049 (1965).
18. K. L. Dhar, O. P. Suri, and K. A. Suri, Indian J. Chem., 29B, 911 (1990).

POLYFUNCTIONAL TRITERPENOIDS FROM THE BARK OF YEDDO SPRUCE

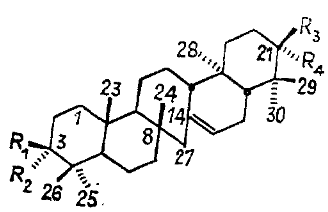
G. F. Chernenko, I. Yu. Bagryanskaya, Yu. V. Gatilov, G. E. Sal'nikov, É. N. Shmidt, and V. I. Mamatyuk

UDC 634.866+547.585.9+548.737

The composition of the polyfunctional triterpenoids of an extract of the Yeddo spruce has been studied. Five serratene triterpenoids have been isolated: 21β-hydroxyserrat-14-en-3-one (I), 3β-hydroxyserrat-14-en-21-one (II), serratenediol (III), episerratenediol (XII), and diepiserratenediol (V) in the form of its acetate. The structures of the compounds were confirmed by ^{13}C NMR spectra and XSA.

We have previously reported the chemical composition of a petroleum ether extract of Yeddo spruce but the polar compounds in it were not investigated [1]. The present work was devoted to their study.

By rechromatography of the total polar compounds we isolated two ketoalcohols (I and II) and three isomeric triterpenediols (III-V) which had been found earlier in bark extracts from various pine species [2-5]. The contradictory statements about the melting points of these compounds found in the literature compelled us to carry out an analysis of the PMR and ^{13}C NMR spectra of compounds (I-V).



I. $R_1+R_2=O$; $R_3=OH$; $R_4=H$
Ia. $R_1+R_2=O$; $R_3=OAc$; $R_4=H$
II. $R_1=OH$; $R_2=H$; $R_3+R_4=O$
III. $R_1=OH$; $R_2=H$; $R_3=H$; $R_4=OH$
IV. $R_1=OH$; $R_2=H$; $R_3=OH$; $R_4=H$
IVa. $R_1=OAc$; $R_2=H$; $R_3=OAc$; $R_4=H$
V. $R_1=H$; $R_2=OAc$; $R_3=OAc$; $R_4=H$
VI. $R_1=H$; $R_2=OCH_3$; $R_3=OAc$; $R_4=H$

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 662-667, November-December, 1992. Original article submitted March 5, 1992.

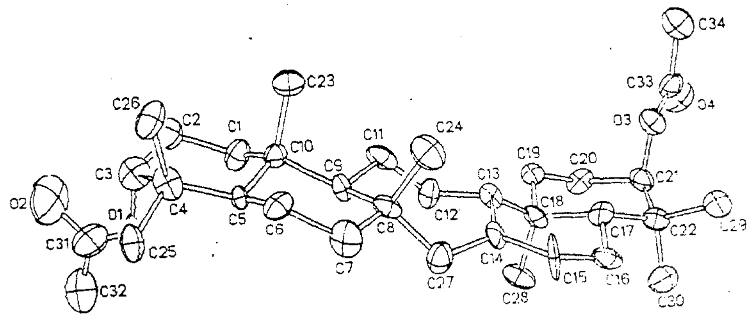


Fig. 1. Crystal structure and relative configuration of 3α, 21β-diacetoxyserrat-14-ene (V).

The ketoalcohols (I) and (II) were serratine derivatives, as was confirmed by their spectral characteristrics, and they differed only by the positions of the functions. The position of the keto group was determined from the sign of the Cotton effect on the optical rotatory dispersion (ORD) curve: for (I) it was positive, and for (II) negative [2]. Analysis of the PMR spectrum of compounds (I) and (II) showed that the signal of the proton geminal to the hydroxy group had the form of a broadened singlet for compound (I) and that of a doublet of doublets for (II), which corresponds to the β-configuration of the hydroxy group [3]. Thus, the hydroxyketones that we have isolated were identified as 21β-hydroxyserrat-14-en-3-one (I) and 3β-hydroxyserrat-14-en-21-one (II) [3].

The most polar fraction of the extract contained diols. We isolated seratenediol (III) — 3β,21α-dihydroxyserrat-14-ene — the spectral characteristics of which were identical with those described in the literature [4] — and diol (IV). A comparison of the PMR spectrum of (IV) with the spectrum of (III) showed that these substances differed by the configuration of one of the hydroxy groups. In compound (IV) the hydroxy group at C_{21} was axial (1 H-21, t, J = 2.5 Hz). Consequently, the diol (IV) isolated was 21-episerratenediol — 3β,21β-dihydroxyserratat-14-ene [3, 5].

On repurification of the polar fractions, followed by their acetylation, we isolated an acetate (V), mp 225-230°C. On the basis of the results of XSA we established for compound (V) the structure of 3α,21β-diacetoxysrrat-14-ene (diepiserratenediol diacetate). The structure of the molecule, the relative configurations of the asymmetric centers, and also the bond lengths are given in Fig. 1. The geometry of the (V) molecule is the usual one. Rings A, B, C, and E have the chair form, and ring D the half-chair form. The acetoxy groups are planar and their orientations with respect to the rings are characterized by C2—C3—O1—C31 and C20—C21—O2—C33 torsional angles of 92(3) and 87(3)°, respectively. There is no reliable information in the literature on the assignment of the signals in the ^{13}C NMR spectra of serratene derivatives, since their interpretation is fairly difficult because of the close values of the chemical shifts of signals with the same multiplicities. To solve this problem, we recorded two-dimensional $^{13}C-^{13}C$ correlation spectra (2D-INADEQUATE) [6] for compound (VI), which we obtained in an amount sufficient for taking such spectra and which has been described in [1]. Interpretation of the literature permitted the unambiguous assignment of the carbon signalsand the confirmation of the structures of compounds (I), (Ia), (II), (IV), (V), and (VI) (Table 1). In a recently published paper [7], assignments were made of the signals of the carbon atoms in the ^{13}C NMR spectra for compound (IV) which agree with the values that we have given, with the exception of the signals of the C_2 and C_{12}; C_8, C_{10}, and C_{18}; C_9 and C_{13}; and C_{11} and C_{20} carbons, which must change places.

Triterpene compounds of the serratene type are frequently encountered in extractive substances of conifer bark [8]. The presence of these compounds characteristic for species of Pinus, Abies, and Picea, is not determined by the growth site and is probably characteristic for the family Pinaceae.

EXPERIMENTAL

Melting points were determined on a Kofler stage. IR spectra were recorded in CCl_4 solution on UR-20 instrument, PMR and ^{13}C NMR spectra were recorded in $CDCl_3$ solution on Bruker AC-200 (200.13 MHz) and Bruker AM-400 (400.3 MHz) instruments (δ scale, internal standard chloroform). The $^{13}C-^{13}C$ two-quantum coherence correlation spectrum was recorded on a AM-400 spectrometer for a solution of 170 mg of compound (VI) in $CDCl_3$ with tuning to the direct $^{13}C-$

TABLE 1. Chemical Shifts (ppm) and Multiplicities of the Signals in ^{13}C NMR Spectra of Compounds (I), (Ia), and (II), (IV), (IVa), (V), and (VI)

C atom	I	Ia	II	IV	IVa	V	VI
1	34,05 t	34,01 t	38,26 t[a]	38,62 t	38,22 t	33,78 t	33,35 t
2	39,45 t	39,45 t	27,43 t[b]	27,14 t[a]	27,59 t[a]	20,08 t	20,05 t
3	218,09 s	218,13 s	78,70 d	78,81 d	80,73 d	78,21 d	85,61 d
4	47,21 s	47,18 s	38,07 s	38,19 s	37,81 s[b]	37,96 s	37,84 s
5	55,12 d	55,02 d	55,61 d	55,77 d	55,73 d	50,45 d	49,95 d
6	20,08 t	20,06 t	18,77 t	18,89 t	18,71 t	18,60 t	18,60 t
7	44,18 t	44,09 t	45,03 t	45,20 t	44,02 t	44,72 t	44,60 t
8	37,34 s[a]	36,98 s	36,99 s	37,41 s[b]	37,07 s[c]	37,25 s	37,17 s
9	62,19 d	62,16 d	62,63 d	62,95 d	62,69 d	62,59 d	62,24 d
10	37,75 s[a]	37,75 s	38,87 s	38,94 s	38,02 s[b]	38,08 t	38,00 s
11	27,56 t	27,56 t	27,09 t[b]	27,56 t[a]	27,09 t[a]	26,94 t	26,91 t
12	25,34 t	25,17 t	25,35 t	25,21 t[c]	25,12 t	25,10 t	25,01 t
13	56,76 d	56,73 d	56,39 d	56,68 d	56,75 d	56,80 d	56,90 d
14	138,05 s	137,99 s	138,21 s	138,46 s	138,32 s	138,42 s	138,49 s
15	122,32 d	122,23 d	121,88 d	122,08 d	121,98 d	121,93 d	121,63 d
16	23,91 t	23,78 t	24,35 t	23,98 t	23,77 s	23,80 t	23,72 t
17	43,27 d	44,26 d	51,11 d	43,41 d	44,36 d	44,35 d	44,25 d
18	35,85 s	35,83 s	36,05 s	35,93 s	35,86 s	35,85 s	35,76 s
19	31,11 t	31,63 t	34,66 t	31,20 t	31,86 t	31,85 t	31,79 t
20	25,17 t	22,86 t	38,50 t[a]	25,44 t[c]	22,89 t	22,89 t	22,83 t
21	76,07 d	78,14 d	218,10 s	76,16 d	78,22 d	78,18 d	78,16 t
22	36,97 s	36,53 s	47,55 s	37,09 s[b]	36,57 s[c]	36,57 s	36,48 s
23	15,70 q	15,78 q	15,62 q[c]	15,66 q	15,74 q	15,49 q	15,65 q
24	19,19 q	19,29 q	19,68 q	19,72 q	19,82 q	19,88 q	19,87 q
25	27,62 q	27,21 q[a]	28,00 q	28,06 q[d]	27,99 q	27,84 q	28,36 q
26	20,90 q	20,87 q[b]	15,31 q[c]	15,33 q	16,47 q	21,71 q[a]	22,38 q
27	56,04 t	56,05 t	55,77 t	56,23 t	56,13 t	56,30 t	56,18 t
28	13,21 q	13,15 q	12,[illegible]3 q	13,23 q	13,15 q	13,12 q	13,0[illegible] q
29	26,83 q	26,67 q[a]	24,43 q	27,62 q[d]	27,23 q	27,22 q	27,19 q
30	21,66 q	21,30 q[b]	21,46 q	21,71 q	21,33 q[b]	21,32 q[a]	21,30 q
O<u>C</u>OCH₃	—	170,67 s	—	—	170,90 s 170,92 s	170,69 s 170,69 s	170,61 s
OCO<u>C</u>H₃	—	21,23 q[b]	—	—	21,21 q[d] 21,21 q[d]	21,22 q[a] 21,22 q[a]	21,20 q
OCH_3	—	—	—	—	—	—	56,76 q

a, b, c, d – the chemical shifts marked by the same letters may change places within a given column.

TABLE 2. Coordinate (in fractions of a cell) of the Nonhydrogen Atoms of Compound (V)

Atom	$\times10^3$	$\times10^3$	$\times10^4$	Atom	$\times10^3$	$\times10^3$	$\times10^4$
O1	218(2)	189(6)	−5395(8)	C16	677(3)	627(4)	−1233(10)
O2	14(5)	115(4)	−6082(13)	C17	492(3)	7[illegible]8(3)	−1047(10)
O3	215(2)	777(2)	11(8)	C18	371(3)	710(4)	−1714(9)
O4	26(2)	919(3)	447(11)	C19	183(3)	743(3)	−1514(9)
C1	88(3)	255(4)	−4050(11)	C20	167(3)	868(3)	−1122(11)
C2	17(3)	145(4)	−4523(11)	C21	286(4)	870(3)	−4[illegible]5(11)
C3	160(4)	90(3)	−4935(14)	C22	481(3)	838(3)	−587(10)
C4	326(3)	47(3)	−4528(11)	C23	162(3)	118(3)	−2989(10)
C5	385(2)	149(3)	−4019(8)	C24	491(3)	247(4)	−2108(11)
C6	549(3)	105(3)	−3584(11)	C25	477(4)	28(4)	−5[illegible]60(12)
C7	628(3)	224(4)	−3244(12)	C26	280(3)	−83(3)	−4216(11)
C8	503(2)	309(3)	−2822(9)	C27	603(3)	445(4)	−2698(11)
C9	325(2)	330(3)	−3202(8)	C28	437(3)	798(3)	−2284(10)
C10	241(3)	210(3)	−3567(10)	C29	579(3)	813(3)	116(10)
C11	199(3)	414(4)	−2757(10)	C30	565(4)	958(4)	−908(13)
C12	249(3)	551(4)	−2591(10)	C31	148(5)	189(5)	−5910(22)
C13	367(2)	570(3)	−1967(8)	C32	179(4)	278(4)	−6406(15)
C14	559(3)	521(3)	−2093(9)	C33	89(4)	817(4)	441(15)
C15	693(3)	560(3)	−1661(10)	C34	34(3)	703(4)	885(11)

^{13}C constants, J_{C-C} = 40 Hz. The time of recording the spectrum was 40 h. All the cross peaks appeared in the spectrum with an adequate signal-to-noise ratio, with the exception of the pair due to the coupling through the double bond. High-resolution mass spectra were obtained on a Finnigan MAT8200, pW instrument. The optical rotatory dispersion in the 210-600 nm region was recorded on a Spectropol I spectropolarimeter. Angles of optical rotation were obtained on a Polamat polarimeter for solutions in chloroform. For adsorption chromatography we used silica gel with a grain size of 71-100 μm, and as solvents petrol ether (bp 40-70°C) (PE) and diethyl ether (DE).

The unsaponifiable neutral substances of an extract of Yeddo spruce bark (8.7 g) were charomatographed on 120 g of SiO_2. For further study we took the polar fraction eluted by DE (3.3 g). This material (3.3 g) was separated chromatographically according to polarity, giving the following reactions enriched with serratene derivatives: 1 (0.6 g), 2 (0.3 g), 3 (0.7 g), and 4 (0.16 g), together with which we isolated β-sitosterol and polymeric products (1.2 g).

21β-Hydroxyserrat-14-en-3-one (I). When fraction 1 (0.6 g) was rechromatographed with DE–PE (1:4), 0.075 g of compound (I) was isolated, with mp 257-259°C (ethyl acetate), $[\alpha]_D^{23}$ + 9° (c 2.99), IR spectrum ($\nu_{max}^{CCl_4}$, cm^{-1}): 1710 (C=O), 3640 (OH), PMR spectrum (AM-400); 0.67, 0.84, 0.85, 0.86, 0.91, 1.00 and 1.05 (each 3H, s, tetiary methyl groups), 2.44 (m, 2H-2), 3.43 (t, J = 2.5 Hz, 1H-21), 5.33 (m, 1H-14). Its ^{13}C NMR spectrum is given in Table 1.

3β-Hydroxyserrat-14-en-21-one (II). Then the same eluting system yielded compound (II) – 0.042 g, mp 253-256°C (acetone), $[\alpha]_D^{22}$ –47° (c 0.17), lit. mp 268-268.5° $[\alpha]_D^{22}$ – 40° [2], mf 268-270° [9], mp 245-247° (ethane) [10] PMR spectrum (AM-400): 0.75, 0.78, 0.81, 0.90, 0.95, 1.02, 1.07 (each 3H, s, tertiary methyl groups), 3.17 (dd, J = 5.0 and 11.5 Hz, 1H-3), 5.33 (m, 1H-14). Its ^{13}C NMR spectrum is given in Table 1. Empirical formula $C_{30}H_{48}O_2$ (found, m/z 440.6354, calculated, 440.3654).

3ρβ-21α-Dihydroxyserrat-14-ene (III). When 0.3 g of the alcohol-containing fraction 2 was chromatographed, DE–PE (1:2) eluted 0.03 g of compound (III), mp 275-279°C, (ethanol), lit. mp 300°C (chloroform–methanol), 282-284°C (benzene–ethanol), $[\alpha]_D^{22}$ – 22° (c 0.7) [4], mp 302-305°, $[\alpha]_D^{21}$ – 19° (c 0.7) [9]. IR spectrum ($\nu_{max}^{CCl_4}$, cm^{-1}): 3610 (OH). PM spectrum: (AC-200): 0.65, 0.75, 0.78, 0.94, 0.95 (each 3H), 0.81 (6H, s, tertiary methyl groups), 3.15 (dd J = 5.5 and 10.0 Hz 1H-3, 1H-21), 5.33 (, 1H-14). Empirical formula $C_{30}H_{50}O_2$ (found, m/z 442.3823; calculated, 442.3811).

3β,21β-Dihydroxyserrat-14-ene (IV). The rechromatography of 0.7 g of fraction 3 with DE–PE (1:1.5) led to the isolation of 0.04 g of compound (Iv), mp 274-277°C (ethanol), $[\alpha]_D^{23}$ – 21° (c 0.74), lit. mp 286-287° [5], 303-308° $[\alpha]_D^{23}$ – 19° (c 1.29) [11]. IR spectrum ($\nu_{max}^{CCl_4}$, cm^{-1}): 3630 (OH). PMR spectrum (AC-200): 0.67, 0.75, 0.78, 0.82, 0.87, 0.91, 0.95 (each 3H, s, tertiary methyl groups), 3.17 (dd, J = 5.5 and 10.0 Hz 1H-3), 3.43 (t, J = 2.5 Hz, 1H-21), 5.31 (m, 1H-14). Its ^{13}C NMR spectrum is given in Table 1. Empirical formula $C_{30}H_{50}O_2$ (found, m/z 442.3821; calculated: 442.3811).

3α,21β-Diacetoxyserrat-14-ene (V). The difficultly separable fraction 4 (0.16 g) was acetylated and, after working up, the reaction mixture was chromatographed. DE–PE (1:6) yielded 0.022 g of compound (V), mp 220-227°C (acetone), lit. mp 240-242°C [5], 240-244°C, $[\alpha]_D^{25}$ – 67° [9]. PMR spectrum (AC-200): 0.67, 0.86, 0.92 (each 3H), 0.82 (12H, s, tertiary methyl groups), 2.04, 2.06 (s, each 3H – $OCOCH_3$), 4.60 (m, 1H-3), 4.64 (m, 1H-21), 5.31 (m, 1H-14).

The X-ray structural analysis of compound (V) was conducted on a Syntex $P2_1$ diffractometer. The crystals were monoclinic: a = 7.517 (9), b = 10.474 (9), c = 19.32 (2) Å, β = 90.67 (8)°, V = 1512 Å, space group $P2_1$, $C_{34}H_{54}O_4$, z = 2, d_{calc} = 1.15 g/cm³, λ CuK_α (graphite monochromator), μ = 0.53 mm^{-1}; specimen dimensions 0.25 × 0.5 × 0.07 mm³. The crystals were of low quality – the widths of the peaks at half-height on ω-scanning amounted to several degrees. The intensities of 3337 reflections in the 2θ < 100° hemisphere were measured by the ω-scanning method (scanning interval 7°). A correction was made for absorption by the SHELX-76 program in the light of the actual dimensions of the specimens. After the averaging of the equivalent reflections, 1672 independent ones were obtained of which 904 were observable (I > 2θ). The structure was interpreted by the method using the SHELX-6 program and was refined by the method of least squares in the anisotropic full-matrix approximation to R = 0.078 and R_W = 0.082, where $W^{-1} = \sigma_F^2 + 0.003\ F^2$. The positions of the hydrogen atoms were calculated geometrically after each cycle of refinement. The atomic coordinates obtained are given in Table 2.

21β-Acetoxyserrat-14-en-one (Ia). The further chromatography of fraction 4 with DE–PE (1:4) yielded 0.06 g of compound (Ia), mp 200-205°C (DE), $[\alpha]_{580}^{23}$ – 1° (c 1.89), lit. mp. 204-207.5° $[\alpha]_D^{22}$ – 1° [2]. PMR spectrum (AC-200): 0.68, 0.82, 0.92, 1.01, 1.06 (each 3H), 0.87 (6H, s, tertiary methyl groups), 2.06 (s, 3H–$OCOCH_3$), 4.66 (t, J = 2.5 Hz, 1H-21), 5.33 (m, 1H-14). Its ^{13}C NMR spectrum is given in Table 1.

3β,21β-Diaetoxyserrfat-14-ene (IVa). The mixture containing compound (IV) (0.028 g) was acetylated, and, after chromatography of the reaction mixture, 0.06 g of compound (IVa) was isolated with mp 221-225°C (acetone), $[\alpha]_D^{23}$ − 11° (c 0.91), lit.: mp 225-229°, $[\alpha]_D$ − 29° (c 2.06) [12]. PMR spectrum (AC-200): 0.68, 0.85, 0.92 (each 3H), 0.82 (12H, s, tertiary methyl groups), 2.02, 2.06, (s, each 3H—$OCOCH_3$), 4.44 (dd, J = 6.0 and 10.0 Hz, 1H-3), 4.66 (t, J = 2.0 Hz, 1H-21), 5.31 (m, 1H-14). Its ^{13}C NMR spectrum is given in Table 1.

LITERATURE CITED

1. G. F. Chernenko, E. E. Ivanova, L. I. Demenkova, and É. N. Shmidt, Khim. Prir. Soedin., No. 5, 645 (1990).
2. J. W. Rowe and C. L. Bower, Tetrahedron Lett., 2745 (1965).
3. R. T. Weston, Austr. J. Chem., 26, 2729 (1973).
4. Y. Inubushi, Y. Tsuda, T. Sano, T. Konita, S. Suzuki, H. Ageta, and Y. Otake, Chem. Pharm. Bull., 15, 1153 (1967).
5. Y. Tsuda and M. Hatanaka, J. Chem. Soc., Chem. Commun., 1040 (1969).
6. T. Bax, R. Freeman, and S. P. Kempsell, J. Am. Chem. Soc., 122, 4849 (1980).
7. Jim-Min Fang, Wei-Yu Tsai and Yu-Shia Cheng, Phytochemistry, 30, 1333 (1991).
8. T. Norin, Phytochemistry, 11, 1231 (1972).
9. A. H. Conner, B. A. Hagasampagi, and J. W. Rowe, Phytochemistry, 19, 1121 (1980).
10. T. H. Rogers and L. R. Rozon, Can. J. Chem., 48, 1021 (1970).
11. J. W. Rowe, Tetrahedron Lett., 34, 2347 (1964).
12. Y. Inubushi and Y. Tsuda, Chem. Pharm. Bull., 13, 104 (1965).

SYNTHESIS OF 3α-HYDROXY-6-KETOBRASSINOSTEROIDS

N. V. Kovganko, O. P. Kananovich, and S. K. Ananich

UDC 547.92

The synthesis has been effected of the new brassinosteroids (22S,23S)-28-homotyphasterol, 24-epityphasterol, and (22S,23S)-24-epityphasterol, which belong to the 3α-hydroxy-6-oxosteroids. For obtaining (22S,23S)-28-homotyphasterol from stigmasterol, a new scheme of synthesis has been developed the key stages of which are the reduction of a 2α,3α-epoxy-6-ketone with lithium tetrahydroaluminate and the selective oxidation of the resulting 3α,6β-diol to the 3α-hydroxy-6-ketone.

The brassinosteroids include phytohormones with a polyhydroxysteroid structure that have been detected in plants in recent years and which possess high plant-growth stimulating activity and increase the resistance of agricultural crops to unfavorable conditions [1]. One of the brassinosteroids is typhasterol, which was isolated in 1983 from the pollen of the cattail *Typha latifolia* [2] and of the pine *Pinus thunbergii* [3]. Continuing an investigation on the synthesis of brassinosteroids and compounds related to them from accessible steroid raw material, we have obtained a number of new brassinosteroid belonging, like typhasterol, to the 3α-hydroxy-6-ketones and being close structural analogs of it. (Formula, top, following page.)

As a result of the solvolysis of the tosylates of the initial sterols β-sitosterol (IIa) and stigmasterol (IIb) and the Jones oxidation of the resulting 6β-hydroxy-3α,5-cyclosteroids we obtained the 6-oxo-3α,5-cyclosteroids (IIIa, b). The opening of the three-membered rings in compounds (IIIa, b) with hydrobromic acid formed the 3β-bromo-6-ketones (IVa, b), the dehydrobrimlination of which with lithium carbonate and bromide in dimethyl formamide led to the corresponding Δ^2-6-ketones (Va, b). The epoxidation of the Δ^2-bond in compound (Va) with m-chloroperbenzoic acid gave a 65% yield of the 2α,3α-epoxy-6-ketone (VIa). Its structure followed from its IR and PMR spectra. In the PMR spectrum of the epoxyketone (VIa) the signals of the vinyl protons at 5.58 and 5.69 ppm characteristic for the spectrum of the initial com-

Institute of Bioorganic Chemistry, Belorussian Academy of Sciences, Minsk. Translated from Khimiya Prirodnykh Soedinenii, No. 6, pp. 667-672, November-December, 1992. Original article submitted February 20, 1992.