rated and chromatographed on Silufol plates (7 × 15 cm) in methyl ethyl ketone saturated with 1% aqueous ammonia, the spots being revealed with aniline phthalate. 2,3,6-Trimethylmannose and 2,3,4,6-tetramethylmannose were used as markers. The intensity of the spot of a dimethylmannose was approximately half that of the spots of the trimethyl- and tetramethylmannoses.

SUMMARY

A glycopeptide containing residues of aspartic acid, glucosamine, and mannose in a ratio of 1:2:5 has been isolated from a pronase hydrolysate of the 7S globulin of cottonseeds, and it has been shown that the mannose chain has a branched structure.

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SYNTHESIS OF 15-CARBOXY-(—)-KAURENES

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From the readily available (—)-kaurene and 6β-acetoxy-18-methoxycarbonyl-(—)-kaurene the corresponding 15-carboxy derivatives have been synthesized. In biotests on the elongation of wheat coleoptiles and the introduction of the synthesis of α-amylase in isolated wheat endosperms, these compounds do not exhibit gibberellin-like activity.

Among growth substance with gibberellin-like activity, considerable interest is presented by helminthosporins — substances with the carbon skeleton of the natural bicyclic sesquiterpenoid helminthosporol [1]. A characteristic feature of the structure of these compounds is the presence in their carbon skeleton of a bridge fragment of the bicyclo-[3,2,1]octane type that is characteristic of gibberellins and their biosynthetic precursors, (—)-kaurenes. In recent years, analogs of helminthosporol and helminthosporic acid have been synthesized many of which possess a considerable gibberellin-like activity [2]. The most active of them have proved to be compounds containing a carbonyl or a carboxyl group in the α position to a nodal carbon atom.

In view of this, and in connection with a further study of the dependence of the activity of this group of substances on their structure, we have synthesized two new 15-carboxy derivatives of (—)-kaurene (XIII and XIV). For this purpose we used (—)-kaurene (I) and 6β-acetoxy-18-methoxycarbonyl-(—)-kaurene (II), obtained previously by the methylation of stachysic acid [3].

The method of synthesizing compounds (XIII) and (XIV) was similar to that proposed previously for helminthosporol derivatives [4], with the difference that to obtain indi-

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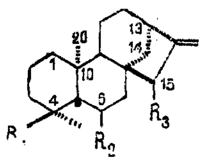
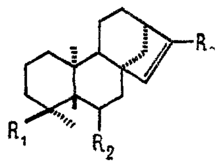
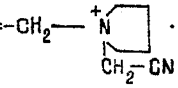
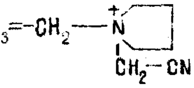
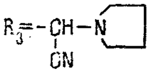
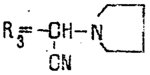


I, II, IX–XV



III – VIII

I. R_1=CH_3, R_2=R_3=H. II. R_1=$COOCH_3$ R_2= β-OAc. R_3= H. III. R_1=CH_3. R_2=H, R_3=CH_3. IV. R_1=$COOCH_3$, R_2=β-OAc, R_3=CH_3. V. R_1=CH_3. R_2=H, R_3=CH_2Br. VI. R_1=$COOCH_3$, R_2=β-OAc, R_3=CH_2Br. VII. R_1=CH_3, R_2=H. R_3=  · Br^-. VIII R_1=$COOCH_3$. R_2=β-OAc R_3=  Br^-. IX. R_1=CH_3, R_2=H, R_3=  X. R_1=$COOCH_3$, R_2=β-OAc, R_3=  XI. R_1= CH_3, R_2=H. R_3=CHO. XII. R_1= $COOCH_3$, R_2= β-OAc, R_3 = CHO. XIII. R_1=CH_3, R_2=H, R_3=-COOH. XIV. R_1= $COOCH_3$, R_2= β-OAc, R_3= COOH. XV. R_1= $COOCH_3$, R_2= β-OAc. R_3=$COOCH_3$

vidual primary bromides, on which the yield of end-products depends, the initial substances (I) and (II) were isomerized to the corresponding isokaurene derivatives (III) and (IV). Then the action of bromosuccinimide on compounds (III) and (IV) gave the primary bromides (V) and (VI). The latter, on interaction with N-cyanomethylpyrrolidine formed the corresponding salts (VII) and (VIII), which, after rearrangement into the nitriles (IX) and (X) followed by hydrolysis, were converted into the corresponding aldehydes (XI) and (XII). Oxidation of the aldehydes with chromium trioxide yielded the 15-carboxy-(—)-kaurenes (XIII) and (XIV). We did not detect the isomers of these compounds with an endocyclic double bond.

The acids synthesized were tested in comparison with (—)-kaurene in the biotest of the induction of the synthesis of α-amylase in isolated wheat endosperms, and also in the wheat coleoptile elongation test. In these tests, compounds (XIII) and (XIV) exhibited no gibberellin-like activity.

EXPERIMENTAL

IR spectra were recorded on a Specord-71 spectrometer and PMR spectra of an RS-60 instrument (working frequency 60 MHz, internal standard tetramethylsilane). The melting points of the substances were determined on a Kofler block. The analyses of all the compounds corresponded to the calculated values.

Isomerization of Compounds (I) and (II). A solution of 300 mg of hydrocarbon (I) in 8 ml of anhydrous benzene was boiled under reflux in a current of argon in the presence of a few crystals of iodine for 12 h. The benzene solution was washed with sodium thiosulfate solution and with water and was dried with sodium sulfate. The residue after the solvent had been distilled off was chromatographed on 12 g of silica gel impregnated with silver nitrate. Petroleum ether containing 10% of benzene eluted 220 mg of the crystalline hydrocarbon (III) with mp 62-63°C (from hexane). IR spectrum (film), cm^{-1}: 820, 1650 (>C=CH—). PMR spectrum (CCl_4), ppm: 0.82 (singlet, 3 H, methyl at C_{10}); 0.96 (singlet, 6 H, methyls at C_4); 1.64 (doublet, 3 H, J = 0.5 Hz, methyl at C_{16}); 5.11 (doublet, J = 0.5 Hz, 1 H at C_{15}).

In the same way, 400 mg of the acetate (II) yielded 350 mg of the isomer (IV) with mp 130-131°C (from petroleum ether–benzene). IR spectrum (CCl_4), cm^{-1}: 1645 (>C=CH—), 1240, 1740 (—$OCOCH_3$ and —$COOCH_3$).

Compounds (V, VI, IX, X, XI, XII, XIII, XIV, and XV) were obtained by methods described by Mander et al. [4].

The Bromide (V). Liquid with the composition $C_{20}H_{31}Br$. IR spectrum (film), cm^{-1}: 840, 1660 (>CH═CH—).

The Bromide (VI). Liquid with the composition $C_{23}H_{33}BrO_4$. IR spectrum (CCl_4), cm^{-1}: 1655 (>CH═CH—), 1240, 1730 (—$OCOCH_3$ and —$COOCH_3$).

The Nitriles (IX) and (X). The bromides (V) (250 mg) and (VI) (400 mg) yielded, respectively (without the isolation of the intermediate salts (VII) and (VIII)): 200 mg of the liquid nitrile (IX), $C_{26}H_{40}N_2$ [IR spectrum (film), cm^{-1}: 880, 1630, 3050 (>C═CH_2), 2200 (—C≡N)] and 300 mg of the nitrile (X), $C_{29}H_{42}N_2O_4$ [IR spectrum (film), cm^{-1}: 900, 1640, 3070 (>C═CH_2), 2200 (—C≡N), 1240, 1740 (—$OCOCH_3$ and —$COOCH_3$)].

The Aldehyde (XI). $C_{21}H_{32}O$. IR spectrum (film), cm^{-1}: 890, 1640, 3050 (>C═CH_2), 1715, 2720 (—CHO).

The Aldehyde (XII). $C_{24}H_{34}O_5$. IR spectrum (film), cm^{-1}: 885, 1655, 3050, (>C═CH_2), 1240, 1740 (—$OCOCH_3$ and —$COOCH_3$), 2700 (—CHO).

Compounds (XIII), (XIV), and (XV). From 120 mg of the aldehyde (XI) was obtained 70 mg of the acid (XIII), $C_{21}H_{32}O_2$, mp 197-198°C (from hexane). IR spectrum (paraffin oil), cm^{-1}: 890, 1650, 3080 (>C═CH_2), 1700 (—COOH).

From 150 mg of the aldehyde (XII) was obtained 100 mg of the acid (XIV), $C_{24}H_{34}O_6$, mp 74-76°C (from petroleum ether—benzene), IR spectrum (KBr), cm^{-1}: 890, 1650, 3080 (>C=CH_2), 1240, 1720 (—$OCOCH_3$, —$COOCH_3$, —COOH). Methyl ester of (XV), $C_{25}H_{36}O_6$, mp 97-98°C (from petroleum ether—benzene). IR spectrum (CCl_4), cm^{-1}: 895, 1660, 3050 (>C═CH_2), 1240, 1730 (—$OCOCH_3$ and —$COOCH_3$). PMR spectrum (CCl_4), ppm: 0.72, 1.17 (singlets, 3 H each, methyls at C_{10} and C_4), 2.00 (singlet, CH_3—CO), 3.56, 3.58 (singlets, 2 COO-CH_3), 4.25 (multiplet, —CHO), 4.83 (multiplet, >C═CH_2).

Determination of the Gibberellin-Like Activities of Compounds (XII) and (XV). After sterilization, 0.5 g of the germ-free endosperms of wheat seeds (variety Svetovaya) was placed in a petri dish and was steeped in sterile water at 3°C for 20 h. The water was poured off, a solution of the substances under test was added to the endosperms, and the mixture was left at 24°C for 36 h. Control endosperms were kept under the same conditions but in water. Then in the germ-free endosperms the activity of the enzyme α-amylase was determined by the method of Smith and Roe in Yurkevich's modification [5].

SUMMARY

The corresponding 15-carboxy derivatives have been synthesized from (—)-kaurene and from 6β-acetoxy-18-methoxycarbonyl-(—)-kaurene. It has been shown that these compounds possess no gibberellin-like activity.

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