THE STRUCTURE OF THE SESQUITERPENE LACTONE SAUPIRIN

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From the epigeal green part of Saussurea neopulchella Lipsch. we have isolated a new sesquiterpene lactone with the composition $C_{19}H_{22}O_6 \cdot H_2O$, mp 75-84°C, $[\alpha]_D^{17}$ + 112° (c 1.7; methanol), and have called it saupirin. The IR spectrum of this substance shows absorption bands at (cm^{-1}) 3590 (OH), 3550 (OH), 3310-3270 (H_2O), 1750 (α-methylene-γ-lactone), 1705 (C = O), and 1660-1650 (C = C). UV spectrum: λ_{max} 202 nm, ε 30,690 (O = C−C = C). The NMR spectrum is shown in Fig. 1.

The hydrogenation of saupirin (I) over a Pt catalyst in ethanol gave two substances: deoxyoctahydrosaupirin (II), $C_{19}H_{30}O_5$, and octahydrosaupirin (V), $C_{19}H_{30}O_6$.

Deoxyoctahydrosaupirin contains one hydroxyl, and it can be acetylated to acetyldeoxyoctahydrosaupirin (III), $C_{21}H_{32}O_6$, the IR spectrum of which lacks the absorption band of a hydroxyl, and oxidized to an oxo compound, oxodeoxyoctahydrosaupirin (IV), $C_{19}H_{28}O_5$, with mp 130-132°C, the IR spectrum showing the absorption band of cyclopentanone (1750 cm^{-1}). Octahydrosaupirin forms diacetyloctahydrosaupirin (VI), $C_{23}H_{34}O_8$.

The hydrogenation of (I) over a Pt catalyst in acetic acid yielded four substances: octahydrosaupirin (V) and deoxyoctahydrosaupirin (II) as two stereoisomeric forms [crystals with mp 145-147°C (IIa) and a vitreous product] and bisdeoxyoctahydrosaupirin (VII), $C_{19}H_{30}O_4$, the IR spectrum of which had no absorption band of an OH group.

What has been said permits the conclusion that the saupirin molecule contains four double bonds and two allyl hydroxyls, one of which is secondary and is present in a five-membered ring.

On saponification, saupirin consumed two molecular proportions of NaOH. The hydrolysis products yielded a dihydroxylactone (VIII), $C_{15}H_{18}O_4$, mp 131.5-133.5°C; its diacetate (IX), $C_{19}H_{22}O_6$, had mp 155-157°C. Such chemical transformations show that saupirin is the ester of a sesquiterpene hydroxylactone $C_{15}H_{18}O_4$ and a hydroxy acid with the composition $C_4H_6O_3$.

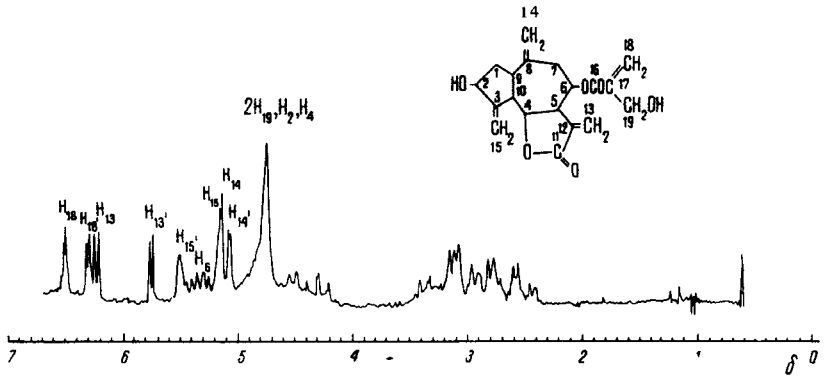

Fig. 1. NMR spectrum of saupirin ([D_5]pyridine, 100 MHz).

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TABLE 1. NMR Spectra of Saupirin and Its Derivatives*

Compound	Protons at							Solvent
	C_2	C_4	C_6	C_{13}	C_{14}	C_{15}	Other C's	
I	4,20—4,90		5,30 m	6,20 d 5,72 d	5,12 d 5,08	5,12 br. s 5,48	6,49—6,28 m (at C_{18}) 4,70 weak d (at C_{19})	C
IV	—	4,32 t†	5,10 sex.	1,00—1,40 (5 CH_3)			—	A
V	4,00—4,30 (2H)		5,10 m	0,90—1,40 (4 CH_3)			3,72 d (2H) at C_{19}	A
VIII	4,26 q	4,05 q	3,90 sex.	6,08 q 6,15 q	4,89 (2,2) d 4,98 (2,2) d	5,23 br. s 5,02		B
IX	5,00 br. sig.	4,31 q	5,00 br. sig.	6,08 (3) d 5,70 (3) d	5,0 (2H) s	5,29 br. s 5,02	2,10 and 1,98 s ($2CH_3CO$)	B
XII	—	3,96 t	—	1,0—1,40 (3 CH_3)				A
XVII	4,31 q	3,96 t	3,72 sex.	1,47 (7) d	4,73 s 4,96 s 5,28 s	5,30 br. s 5,05		A
XVIII	6,11 m	4,15 t	—	1,31 (6) d	5,15 s	2,35 s		A
XIX	Unresolved signal			0,90—1,40 ($3CH_3$)		1,88 s	3,80 m (2H) at C_{19}	A
XXI	5,65 m	4,02 t	4,00 m	1,55 (7) d	1,10 (6) d	1,67 s	4,75 br. sig at C_1	C

* The figures are given in ppm; the coupling constants are given in brackets and are expressed in Hz.
† s – singlet; br. sig. – broadened signal; q – quartet; sex. – sextet; m – multiplet; t – triplet; d – doublet; A – deuterochloroform; B – deuteroacetone; C – deuteropyridine.

The hydrogenation of (VIII) over a Pt catalyst in ethanol formed the hexahydro derivative (X), $C_{15}H_{24}O_4$, which, on acetylation, gave a diacetate (XI), $C_{19}H_{28}O_6$, and on oxidation gave a dioxolactone (XII), $C_{15}H_2OH_4$, as two isomers with mp 133-136°C and 175-185°C. Their IR spectra were almost identical and contained the absorption bands of cyclopentanone (1725 cm^{-1}) and cycloheptanone (1710 cm^{-1}).

These results confirm the presence in (VIII) of three double bonds and two secondary hydroxyls, one of which appeared in the hydrolysis of the acyl residue, and also the fact that the latter is present in a seven-membered ring in (I).

The carbon skeleton of saupirin was investigated by dehydrogenation over selenium. The dehydrogenation of (I, II, V, and VIII) gave chamazulene (XIII) in low yield.

To isolate furanoazulenes and thus to determine not only the nature of the carbon skeleton but also the position of the lactone ring, we dehydrogenated the products obtained by the treatment of the dihydroxyhexahydrolactone (X) with sodium tetrahydroborate. From the dehydrogenation products we isolated artemazulene (XIV), forming a trinitrobenzene derivative with mp 195-196°C.

Chamazulene and artemazulene can be obtained by the dehydrogenation of guaianolides, ambrosanolides, and germacranolides. An ambrosane skeleton for saupirin is excluded since the NMR spectrum of (I) does not have the characteristic methyl singlet.

From biogenetic considerations [1, 2] it is possible to assume either a germacrane or a guaiane skeleton (difference 2H) for saupirin.

Cases of the rearrangement of a germacrane skeleton into a guaiane skeleton are known, but in our experiments five- and seven-membered rings were found in all derivatives. In addition to this, if (I) had a germacrane skeleton, there should be an additional double bond; however, the NMR spectrum and chemical transformations do not confirm this.

Saupirin does not give a molecular peak in the mass spectrum, but the dihydroxylactone (VIII) gives a molecular peak at 262. Consequently, saupirin may be regarded as a guaianolide.

All four double bonds in saupirin are terminal, as follows from the NMR spectra of (I) and its derivatives. The products of the hydrogenation of saupirin do not give signals of exocyclic methylene groups (Table 1) but have the signals of methyl groups[$4CH_3$ in (V) and $5CH_3$ in (IV)]. Compound (VIII) has only three exocyclic methylene groups, and therefore one terminal double bond is present in the acyl residue.

The NMR spectrum of (I) also shows the signal of protons of a $CH_2OH-C=C$ group (s, 4.70 ppm), while in (V), as was to be expected, this signal has shifted upfield (d, 3.72 ppm). There are no signals of CH_2OH groups in the NMR spectra of (II) and (IV), but an additional signal of methyl protons appears; i.e., CH_2OH has been reduced to CH_3, which is in harmony with the chemical facts given above. The NMR spectrum of (VIII) lacks the signals of protons of a hydroxymethylene group and the signals of protons of a second exocyclic methylene group conjugated with a carbonyl which were observed in (I). Thus, saupirin is a hydroxymethylacrylate.

The acyl residue is in the β position to an exocyclic methylene of a γ-lactone, as is shown by the NMR spectra of (I, VIII, and IX). The question of the influence of β substituents on the nature and position of the signals of the protons of an α-methylene-γ-lactone has been discussed thoroughly in the literature [3]: when an OH is present in this position, the signals of the protons of the exocyclic methylene are quartets with small distances between them; on acylation these distances increase markedly and the signals become doublets (see Fig. 1 and Table 1). Previous experiments gave us convincing information on the presence of the second hydroxyl in the five-membered ring in the α position to the double bond, i.e., at C_2. Unfortunately, in the NMR spectrum of saupirin, H_2 does not give sharp lines, which would have enabled an idea to be obtained of the position of the hydroxyl.

The dihydroxylactone (VIII) was reduced in the presence of a small amount of sodium tetrahydroborate. In complete agreement with the literature [4, 5], reduction of the methylene group conjugated with the carbonyl of the γ-lactone took place. In addition, product (XVII), $C_{15}H_{20}H_4$, mp 172-173°C, was obtained. The NMR spectrum of the latter (see Table 1) showed the signals of two exocyclic methylenes and one methyl adjacent to C = O (d, 1.47 ppm, Fig. 2). Compound (XVII) was oxidized with chromium trioxide in an acid medium to the dioxo derivatives (XVIII), $C_{15}H_{16}O_4$, with mp 221°C (decomp.). Its IR and UV spectra show that the substance contains an α,β-cyclopentenone system (ν_{max} 1690 cm^{-1} and λ_{max} 232 nm,

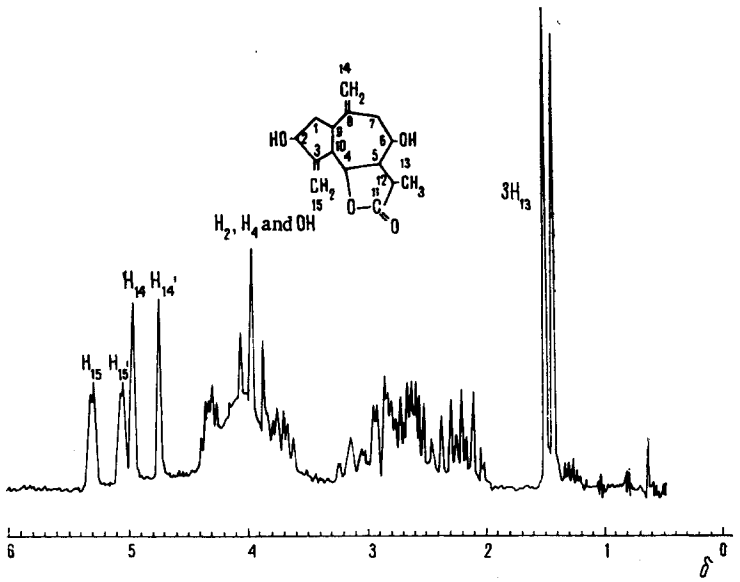


Fig. 2. NMR spectrum of substance (XVII) ($CDCl_3$, 100 MHz).

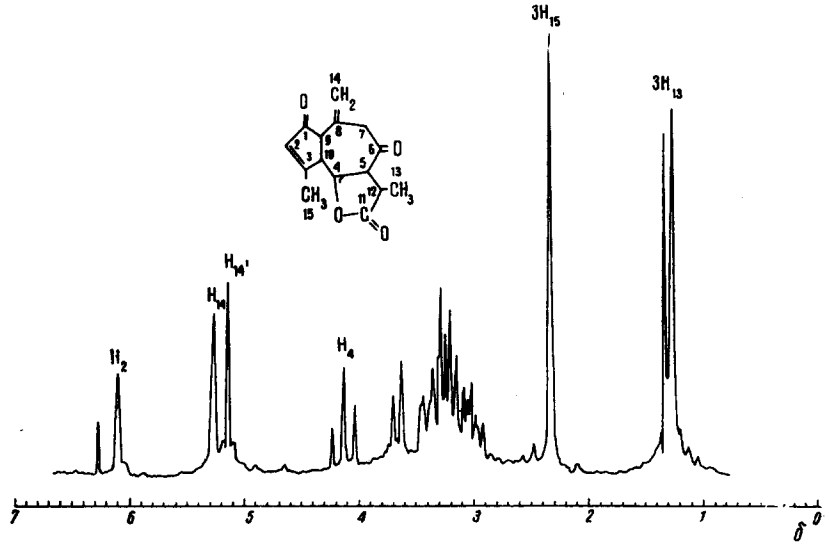


Fig. 3. NMR spectrum of substance (XVIII) ($CDCl_3$, 100 MHz).

ε 5528), the formation of which is possible only with a rearrangement of the double bond and the hydroxyl. In actual fact, the NMR spectrum of (XVIII) had no signals of one of the two exocyclic methylenes present in (XVII), but a new signal of a methyl group on a double bond was observed; in addition to this, there was the signal of a vinyl proton (Fig. 3).

A proof of a rearrangement in the five-membered ring is the production of substance (XIX) by the hydrogenation of saupirin over a Ni catalyst and its oxidation to (XX). The UV spectrum of (XX) has a maximum at 233 nm (ε 5354) which shows the presence of an α,β-cyclopentenone grouping in its molecule. We observed migration of an exocyclic double bond into the five-membered ring with a rearrangement of the hydroxyl when (VIII) was hydrogenated over a Ni catalyst; this process gave, in addition to (X), compound (XXI), $C_{15}H_{22}O_4$, mp 170-174°C (decomp.), ν_{max} 3360 cm^{-1} (OH), 1775 cm^{-1} (γ-lactone), 1660 cm^{-1} (C = C); NMR spectrum: s, 1.87 ppm – CH_3–C = C (see Table 1).

On the basis of the facts given above, we propose structure (I) for saupirin. In its composition, IR spectrum, melting point, and structure, product (IIa) corresponds to one of the products of the hydrogenation of cynaropicrin – a hydroxy ester of the lactone (II) [6]. We have also isolated saupirin from Saussurea pulchella Fisch. We have detected no other lactones in S. pulchella or S. neopulchella.

EXPERIMENTAL

Isolation of Saupirin from Saussurea neopulchella Lipsch. The epigeal green part collected by A. I. Shreter in the Maritime Territory (Anuchinskii region) in the flowering phase (1.0 kg) was covered with hot water (75°C) and steeped for 30 min. Extraction was repeated three times. The saupirin was extracted from the aqueous infusion with chloroform; removal of the solvent gave a crystallizing resin. The crystals were washed with ether and were then recrystallized three times from ethyl acetate. Large colorless crystals with mp 74-85°C deposited. After drying in a dark desiccator over H_2SO_4 for three days – mp 75-84°C.

Found %: C 62.60; 62.76; H 6.58; 6.72; H_2O (Karl Fischer) 4.19. $C_{19}H_{22}O_6 \cdot H_2O$
Calculated %: C 62.62; H 6.64; H_2O 4.90.

After drying under the same conditions for ten days – mp 76-85°C.

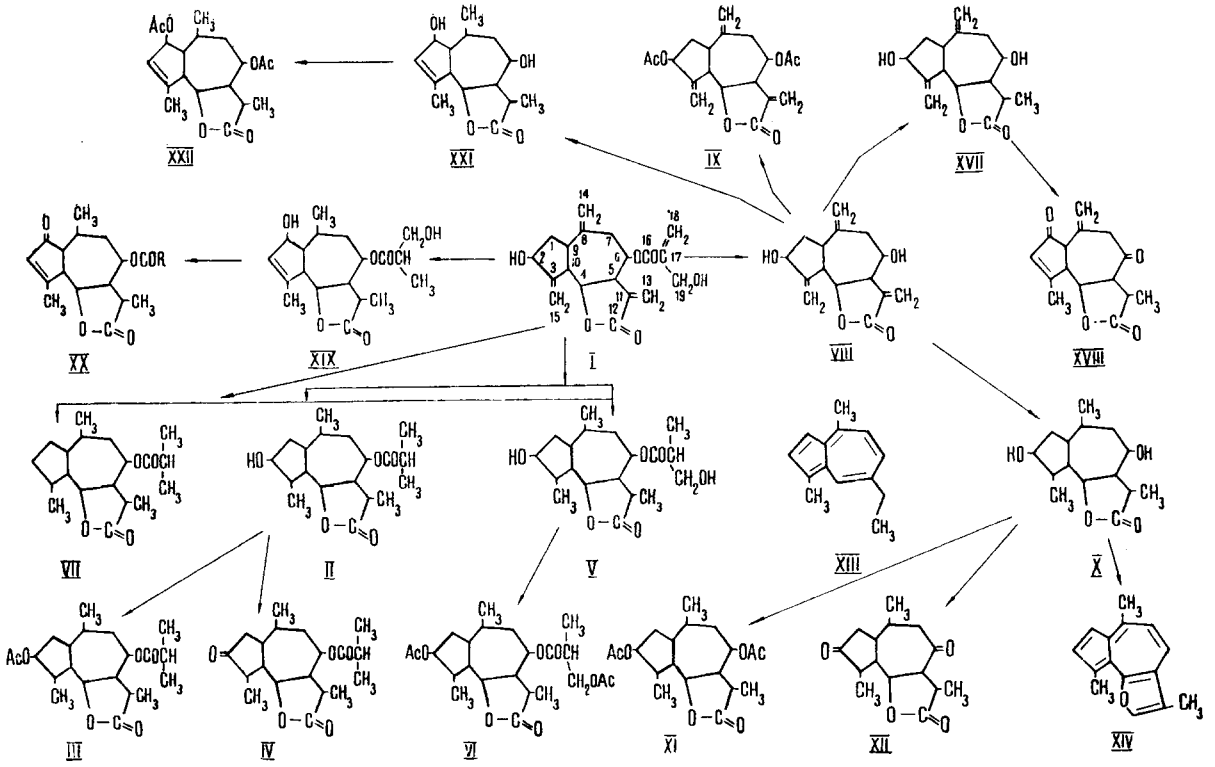
Found %: C 63.29; 63.08; H 6.77; 6.84.

After drying for 17 days, the saupirin was converted into an amorphous yellow powder which did not melt below 300°C. The change was irreversible.

Found %: C 60.16; 59.60; H 6.06; 6.11.

Similar results were obtained on drying in a desiccator over P_2O_5 or $CaCl_2$, these changes taking place most slowly over $CaCl_2$. When fresh samples of saupirin were chromatographed in various solvent systems in a thin layer of neutral alumina (activity grade IV), a single spot was always found. Column chromatography on neutral alumina (activity grade IV) gave a substance with the initial constants.

In view of the ready susceptibility to changes, we worked with a sample which had been dried over $CaCl_2$ for ten days and had then been stored in a darkened desiccator without adsorbents; mp 75-84°C.



Saupirin from Saussurea pulchella Fisch. A plant gathered by the botanist M. G. Pimenov in the Maritime Territory (Chuguevskii region) in 1963 in the budding phase was used. Saupirin was isolated by the method described previously [7, 8]. Colorless crystals deposited with mp 74-85°C (from aqueous ethanol). After drying under the same conditions – mp 75-84°C. The IR and NMR spectra were similar to

those of the previous sample of saupirin. We did not find the lactone saurin isolated previously from this sample of raw material [7].

Found %: C 62.91; 62.69; H 6.81; 6.46. $C_{19}H_{22}O_6 \cdot H_2O$. Calculated %: C 62.62; H 6.64.

Hydrogenation of (I) over Pt in Ethanol. When 4.0 g of saupirin in 50 ml of ethanol was hydrogenated in the presence of 0.1 g of PtO_2, 4.5 moles of hydrogen was absorbed. After the catalyst and ethanol had been eliminated, a colorless viscous liquid was obtained (according to TLC – two spots with R_f 0.8 and 0.3 in ether). It was chromatographed on 50 g of Al_2O_3 (activity grade IV, neutral), and eluted with ether, giving two vitreous substances: deoxyoctahydrosaupirin (II), $C_{19}H_{30}O_5$, with R_f 0.8, yield 1.4 g, IR spectrum: ν_{max} 3520-3320 cm^{-1} (OH), 1780-1710 cm^{-1} (C = O); and octahydrosaupirin (V), $C_{19}H_{30}O_6$, with R_f 0.3, yield 2.1 g, ν_{max} 3620, 3520 cm^{-1} (OH), 1775 cm^{-1} (γ-lactone), 1740 cm^{-1} (OCO).

The analytical results for deoxyoctahydrosaupirin and all the subsequent derivatives corresponded to the calculated figures.

Acetylation of (II). A solution of 0.5 g of substance (II), 5 ml of pyridine, and 10 ml of acetic anhydride was left at room temperature for 10 h and was then diluted with water. The reaction product was extracted with ethyl acetate, and the extract was washed with 10% HCl and with water. Elimination of the solvent gave about 0.5 g of an almost colorless vitreous product (III), $C_{21}H_{32}O_6$, R_f 0.65 [TLC, benzene–ethanol (9 : 1)]. ν_{max} 1780 cm^{-1} (γ-lactone), 1750-1740 cm^{-1} (OCO).

Acetylation of (V). The acetylation of 0.2 g of (V) was performed in the same way as in the preparation of (III). Compound (VI), $C_{23}H_{34}O_8$, was isolated in the form of a vitreous product with R_f 0.65 [TLC, benzene–ethanol (9 : 1)], ν_{max} 1780, 1750-1740 cm^{-1}.

Oxidation of (II). A mixture of 0.4 g of (II), 0.4 g of CrO_3, and 20 ml of 90% CH_3COOH was kept at +5°C for a day and was then diluted with water and extracted with chloroform, and the extract was washed with water. A vitreous mass was isolated which, from ethereal solution, gave colorless crystals of (IV), $C_{19}H_{28}O_5$, mp 130-132°C, ν_{max} 1780 cm^{-1} (γ-lactone), 1750 cm^{-1} (cyclopentanone), and 1730 cm^{-1} (OCO).

Hydrogenation of (I) over Pt in CH_3COOH. The hydrogenation of 3.37 g of saupirin was performed in 100 ml of glacial acetic acid in the presence of 0.1 g of PtO_2. (Five moles of hydrogen was consumed.) The reaction mixture was diluted and neutralized with sodium carbonate, and the reaction product was extracted with chloroform and washed with water. The extract yielded 3.2 g of a viscous colorless liquid which on TLC in the benzene–ethanol (9 : 1) system gave three spots. It was chromatographed on 85 g of neutral Al_2O_3 (activity grade IV). Elution with ether gave seven fractions [fractions 5, 6, and 7 gave a single spot with R_f 0.3 on TLC in the benzene–ethanol (9 : 1) system; while fractions 1-4 gave two spots on TLC]. These fractions were rechromatographed under the same conditions, and three substances were isolated, with R_f 0.9 and 0.5 (both viscous colorless liquids) and R_f 0.45 (colorless crystals). In all, four substances were obtained.

Bisdeoxyoctahydrosaupirin (VII) – colorless vitreous product with the composition $C_{19}H_{30}O_4$, R_f 0.9 (yield 0.1 g), ν_{max} 1775 cm^{-1} (γ-lactone), 1740 cm^{-1} (C = O).

Deoxyoctahydrosaupirin – colorless vitreous product (yield 1.0 g), identical with (II) in composition and IR spectrum.

Deoxyoctahydrosaupirin (IIa) – colorless acicular crystals with the composition $C_{19}H_{30}O_5$, mp 145-147°C (from ether), yield 0.1 g, R_f 0.45. IR spectrum, ν_{max}, cm^{-1}: 3370 (OH), 1780 (γ-lactone), 1735 (OCO).

Octahydrosaupirin – vitreous product with R_f 0.3 (yield 1.3 g). Identical with (V) in composition and IR spectrum.

Hydrogenation of (I) over a Ni Catalyst. The hydrogenation of 3.0 g of (I) was performed in 50 ml of ethanol over Raney nickel. The amount of hydrogen absorbed was 3 moles. After the catalyst and solvent had been removed, a vitreous product was formed – (XIX), $C_{19}H_{28}O_6$, R_f 0.3 [TLC in the benzene–ethanol (9 : 1) system], ν_{max} 3500-3400 cm^{-1} (OH), 1770 cm^{-1} (γ-lactone), 1750 cm^{-1} (OCO), 1650 cm^{-1} (C = C).

Oxidation of (XIX). A mixture of 0.4 g of (XIX) and 0.4 g of CrO_3 in 50 ml of 90% CH_3COOH was kept at 22°C for 2 h and then, as in the preparation of (IV), 0.15 g of substance (XX) was isolated from the reaction products. UV spectrum: λ_{max} 233 nm (ε 5354).

Hydrolysis of Saupirin. Isolation of the Dihydroxylactone (VIII). A. A mixture of 0.1720 g of saupirin, 10 ml of ethanol, and 15 ml of a 0.1 N solution of NaOH was heated in the boiling water bath for 20 min and cooled, and the excess of alkali was back-titrated with 0.1 N H_2SO_4 solution. The molecular weight found was 363.

B. A mixture of 2.0 g of saupirin and 100 ml of 4% KOH solution was kept at room temperature until the crystals had dissolved completely and it was then acidified with 10% H_2SO_4 solution to pH 1 and exhaustively extracted with ethyl acetate. The extract was washed three times with 5% $NaHCO_3$ solution and then with water. Elimination of the solvent gave almost colorless crystals of (VIII), $C_{15}H_{18}O_4$, mp 131.5-133.5°C (from ether), mol. wt. 262 (mass spectrometrically). Yield 0.9 g, ν_{max} 3340 cm^{-1} (OH), 1740 cm^{-1} (α-methylene-γ-lactone), 1645 cm^{-1} (C = C), λ_{max} 199 nm (ε 17,994).

C. A mixture of 0.5 g of saupirin, 25 ml of dioxane, and 25 ml of 1 N KOH solution was heated in the boiling water bath for 1 h, cooled, acidified with 10% H_2SO_4 solution to pH 1, and extracted with ethyl acetate, and the extract was washed with water. Crystals of (VIII) deposited with mp 130-132.5°C (from ether); yield 0.1 g. The IR spectrum was identical with that of the substance in experiment B.

Acetylation of (VIII). A mixture of 0.77 g of (VIII), 7 ml of acetic anhydride, and 14 ml of pyridine was left in the cold for 48 h and was then diluted with water and extracted with chloroform. The extract was washed with 10% HCl solution and with water. After elimination of the solvent and recrystallization from ethanol, colorless crystals of (IX), $C_{19}H_{22}O_6$, were obtained with mp 155-157°C, ν_{max} (cm^{-1}) 1775 (γ-lactone), 1750, 1260, 1240 ($OCOCH_3$), and 1650 (C = C).

Hydrogenation of (VIII). The hydrogenation of 1.96 g of (VIII) was performed in 50 ml of ethanol in the presence of 0.1 g of PtO_2. The amount of hydrogen consumed was 3 moles. Elimination of the solvent gave the vitreous substance (X), $C_{15}H_{24}O_4$, R_f 0.45 [TLC; benzene–ethanol (9 : 1)].

Acetylation of (X). A mixture of 0.2 g of (X), 4 ml of pyridine, and 2 ml of acetic anhydride was heated at 50°C for 2 h. The reaction product was treated in the same way as for the preparation of (IX). This gave the vitreous product (XI), $C_{19}H_{28}O_6$, R_f 0.85 [TLC; benzene–ethanol (9 : 1)].

Oxidation of (X). A mixture of 0.4 g of (X) and 0.4 g of CrO_3 in 20 ml of 90% CH_3COOH was kept at +5°C for 18 h and was then diluted with water and extracted with chloroform, and the extract was washed with 5% $NaHCO_3$ solution and with water. Elimination of the chloroform gave a mixture of two substances with R_f 0.47 and 0.52 (TLC; ether). The addition of ether yielded crystals of (XII), $C_{15}H_{20}O_4$, mp 133-136°C, ν_{max} 1780 cm^{-1} (γ-lactone), 1725 cm^{-1} (cyclopentanone), and 1710 cm^{-1} (cycloheptanone). From the mother liquor were obtained crystals with the composition $C_{15}H_{20}O_4$, mp 175-185°C (from ether). Its IR spectrum was similar to that of compound (XII).

Hydrogenation of the Dihydroxylactone (VIII) over a Ni Catalyst. The hydrogenation of 1.32 g of (VIII) was performed in 60 ml of ethanol over a Raney nickel catalyst. The amount of hydrogen consumed was 2.2 moles. Removal of the catalyst and the solvent left a crystalline mixture of two substances with R_f 0.9 and 0.4 (TLC; ether). The crystals were washed repeatedly with ether, giving substance (XXI), $C_{15}H_{22}O_4$, mp 174°C (decomp.), R_f 0.4, ν_{max} 3360 cm^{-1} (OH), 1775 cm^{-1} (γ-lactone), 1660 cm^{-1} (C = C).

Acetylation of (XXI). A mixture of 0.05 g of (XXI) 1 ml of acetic anhydride, and 2 ml of pyridine was left overnight and was then treated as in the preceding experiments. This gave a faintly colored vitreous product, (XII), with the composition $C_{19}H_{26}O_6$.

Reduction of (X) with $NaBH_4$ and Subsequent Dehydrogenation over Se. A mixture of 0.4 g of (X) in 5 ml of methanol and 1.0 g of $NaBH_4$ in 20 ml of methanol was left until the reaction ceased (3 h), and was then diluted with water, acidified with 10% H_2SO_4 to pH 1, and extracted with chloroform, and the extract was washed with water. After the elimination of the solvent, a vitreous substance was obtained (TLC; mixture of three substances with R_f 0.37, 0.48, and 0.57), the IR spectrum of which lacked carbonyl absorption bands. The products obtained were dehydrogenated over 0.6 g of selenium at 280-325°C for 26 min. The reaction product was extracted with petroleum ether. This yielded a viscous violet liquid – artemazulene (XIV) – which on the addition of a solution of trinitrobenzene gave crystals in the form of black needles with mp 195-196°c (from ethanol). A mixture with an authentic sample showed no depression of the melting point.

Reduction of (VIII) with $NaBH_4$. A mixture of 1.0 g of (VIII) in 15 ml of methanol and 0.5 g of $NaBH_4$ in 15 ml of ethanol was kept at room temperature for 1.5 h. Then it was diluted with water, acidified with 10% H_2SO_4, and extracted with ethyl acetate, and the extract was washed with water. The solvent was driven off and the crystals were washed with ether to give substance (XVII), $C_{15}H_{20}H_4$, mp 172-173.5°C, ν_{max} (cm^{-1}) 3400, 3420 (OH), 1745 (γ-lactone), 1640 (C = C).

Oxidation of (XVII). A solution of 0.12 g of (XVII) in 10 ml of acetone was treated dropwise at 0°C with an 8 N solution of chromic acid until a permanent coloration appeared, and it was then diluted with water and extracted with ethyl acetate, after which the extract was washed with water, with 5% $NaHCO_3$ solution, and again with water. After the solvent had been distilled off, a colored vitreous product remained. This was chromatographed on Al_2O_3 (activity grade IV) and the colorless crystals were washed with ether to give substance (XVIII), $C_{15}H_{16}O_4$, mp 221°C (decomp.), ν_{max} (cm^{-1}) 1785 (γ-lactone), 1720 (cycloheptanone), 1690 (cyclopentanone), 1640 and 1620 (C = C).

CONCLUSIONS

A new sesquiterpene lactone, saupirin, has been isolated from the epigeal green part of Saussurea neopulchella Lipsch. and Saussurea pulchella Fisch., and structure (I) has been proposed for it.

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