The Structure of Phloropyron

Aneri Penttilä and Jacobus Sundman

The Research Laboratories, Medica Ltd., Helsinki, Finland

Phloropyron (X), a phloroglucinol derivative isolated from Dryopteris fern, has been shown to be a dimerous compound wherein 3-butrylphlicin acid is tied to 6-propyl-2,3-dihydropyrano-2,4-dione by means of a methylene bridge.

The structures of the following naturally occurring phloroglucinol derivatives from Dryopteris species have been reported and described by several investigators:

- aspidinol (I) — Boehm ¹, Robertson and Sandrock ²
- albaspidin (II) — Boehm ³
- aspidin (III) — Riedl and Mitteldorf ⁴
- flavaspic acid (IV) — McGookin, Robertson and Simpson ⁵, Riedl ⁶
- desaspindin (V) — Büchi, Aebi and Kapoor ⁷
- filixic acid (VI) — Riedl ⁶, Chan and Hassall ⁸.

A new compound, for which we suggest the name phloropyron, has now been isolated and its structure has been proved by identifying its decomposition products and by synthesis.

In earlier reports concerning phloroglucinol derivatives from Dryopteris species two other substances are of interest, i.e. aspidin and polystichinin. No attempts to explain the structures of these compounds have been made.

In 1897, Boehm ⁹ described aspidin as a colourless crystalline substance, m.p. 110°C, slightly soluble in alcohol and petroleum ether, soluble in sodium carbonate, the solution first being colourless and then turning dark red in a few hours. The addition of dilute ferric chloride to an alcoholic solution of aspidin gives a green colour which rapidly changes to dark brown.

In 1898, Poulsson ¹⁰ isolated from Aspidium spinulosum a substance melting at 110.5°C, for which he proposed the name polystichinin. The properties of his compound agree, in part fairly well with those of aspidin. However, minor differences in crystal form and ferric chloride reaction forced him to doubt the identity of polystichinin with aspidin.

About forty years later Maizite ¹¹ isolated from Nephrodium austriacum a substance melting at 112—113°C. On the basis of its physical and chemical
properties he assumed it to be identical with aspidin and polystichinin mentioned above.

In more recent investigations, Mühlemann 12, Widén 13, Büchi, Aebi and Kapoor 7 and Aho 14 report that they have not been able to find aspidin. According to Büchi 7 the existence of aspidin is highly doubtful; he supposed that the earlier investigators actually dealt with a stable mixture of aspidin and albaspadin, melting sharp at 110—112°, rather than with a genuine compound.

The properties of our phloropyron, including melting point, solubility and colour reactions, agree to such an extent with those of Boehm's aspidin that there seems to be little doubt of their identity. In spite of this we have chosen a new name in order to emphasize the wide structural differences between phloropyron and the other phloroglucinols mentioned above. The impossibility of phloropyron being a mixture of aspidin and albaspadin is evidenced by our results and can, moreover, easily be proved by paper chromatographic separation 15, the \( R_F \)-values being: aspidin 0.73, albaspadin 0.56 and phloropyron 0.28.

That also the polystichinin of Poulsans is identical with phloropyron was found out by preparing an aniline derivative of phloropyron. According to Poulsans 16 the aniline derivative of polystichinin had a m.p. of 110—113°; the corresponding compound derived from phloropyron melted at 111—112°. Though the analytical data of polystichinin as reported by Poulsans 16 are in rather poor agreement with our data on phloropyron there is, however, no reason to question the identity of these two substances.

Phloropyron was found in Dryopteris austriaca (Jacq.) Woynar in amounts of 0.2% as calculated on air dried rhizomes. In Dryopteris filix mas (L.) Schott it could not always be detected, but when present, it amounted to 0.10—0.15%. The figures mentioned are based on semi-quantitative paper chroma-

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**Fig. 1.** Ultraviolet absorption spectra of flavaspidic acid (A), phloropyron (B), triacetic lactone (C) and 6-propyl-2,3-dihydropyran-2,4-dione (D) in ethanol (99.5%).

tographic analyses of non-alkali treated phloroglucinol concentrates. At their best the amounts of phloropyron actually isolated from the rhizomes rise to one half of the figures above.

Phloropyron, together with other phloroglucinol substances, was obtained from Dryopteris species by extraction, the extract was freed of lipid material and phloropyron was separated from the other phloroglucinols by reextraction. After several recrystallisations from ethanol, phloropyron was obtained in a pure state as white needles melting at 111—112°. It was a monobasic acid the analytical data of which agreed with the formula C_{21}H_{39}O_{7}. Molecular weight determinations confirmed it as 390. Phloropyron failed to give the methoxyl group reaction. In chloroform solution it proved to be optically inactive. The ultraviolet spectrum of phloropyron resembled that of flavaspidic acid (IV) (Fig. 1.); it did not supply further information.

The alkaline cleavage of phloropyron yielded butyric acid, propionic acid, acetic acid and filicinic acid (VII); other phloroglucinols could not be found. If the alkaline degradation was carried out under very mild conditions butyrylfilicinic acid (VIII) could be identified by paper chromatographic separation.

The amount of fatty acids, calculated as butyric acid, obtained by the alkaline decomposition was about 45 % of phloropyron. Paper chromatographic separation of the fatty acids indicated that the major part consisted of butyric acid, but small amounts of acetic acid and propionic acid could always be found.

Rather different results were obtained by the acidic degradation of phloropyron. When warmed with conc. sulphuric acid only butyric acid could be identified, the same amounting to about 22 %. A new crystalline compound could also be isolated from the sulphuric acid solution. The analytical data for this compound agreed with the formula C_{17}H_{30}O_{6}, indicating that it probably is a product resulting from phloropyron by removal of the butyric acid moiety. This new compound, desbutyrophaorphloropyron (IX), had a m.p. of 161—162°.

When desbutyrophaorphloropyron (IX) and 3-butyrylfilicinic acid (VIII) were dissolved in potassium hydroxide (1 %) and the solution was treated with formaldehyde, phloropyron (X) could be identified by paper chromatography among the products formed. Consequently, butyrylfilicinic acid partly replaced the filicinic acid component in the desbutyrophaorphloropyron molecule. The reaction can be interpreted as evidence in support of phloropyron being a methylene compound with butyrylfilicinic acid as one member. Further investigations were concentrated on the isolation of the second half of the phloropyron molecule.

By gentle alkaline treatment with dilute sodium carbonate, phloropyron was broken up and the expected new compound isolated from the solution by extraction. In order to obtain this substance, hereinafter designated as PPD, in a pure state, a chromatographic separation through a column filled with perlone powder proved to be effective. After recrystallisations PPD had a melting point of 93—94°. It is a monobasic acid forming long white needles, soluble in hot water, very soluble in ethanol and aceton and slightly soluble in ether. The ferric chloride reaction is yellowish brown.

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The formula of PPD, C₈H₁₀O₄, satisfied the requirements of an isomer of fiineic acid (VII) but its properties differed widely from those typical of phloroglucinols 19.

By catalytic hydrogenation of PPD carried out in the Warburg apparatus 20 one mole of hydrogen was absorbed indicating one double bond. The hydrogenation product was not isolated. By diazomethane treatment PPD gave a methoxyl compound containing one methoxyl group. With diazoaminobenzene yellow needles were obtained, m.p. 134—135°.

Boiling of PPD with dilute sodium hydroxide resulted in total decomposition of the molecule. By steam distillation a mixture of ketonic compounds could be isolated. After acidifying the product the volatile acids were distilled off. The ketones were converted to the corresponding dinitrophenylhydrazones, from the mixture of which the derivatives of acetone and methyl propyl ketone were identified. The volatile acids were separated by a paper chromatographic analysis 17. Butyric acid and acetic acid were identified and, furthermore, the butyric acid was proved by gas chromatography to be the n-isomeric one.

When boiled with dilute acids PPD decomposed to carbon dioxide and a volatile compound which could be isolated by steam distillation. This compound gave a greyish blue copper complex, m.p. 167—169°, which easily hydrolysed to give the decomposition products already mentioned, namely butyric acid, acetic acid, acetone and methyl propyl ketone. It was, consequently, a β-diketone and was identified as heptane-2,4-dione 21 by melting point and mixed melting point determinations of the copper complex of synthetic heptane-2,4-dione.

Considering the instantaneous decarboxylation on acidic hydrolysis of PPD it is believed that the carboxyl group is in β-position to either oxo-group in heptane-2,4-dione, this obviously leading to an enol lactone structure for PPD. The relatively high stability of PPD permitted us to ignore the possibilities arising from a β-lactone structure, thus leaving only the δ-lactones to be
taken into consideration. Of the two possibilities, the δ-lactone derived from heptane-2,4-dione with the carboxy group in position 5 had a m.p. of 185—
188⁰ 22-24 and, consequently, was out of question.

The facts thus obtained seemed to be sufficient for formulating PPD as
the δ-lactone of 3-oxo-5-hydroxy-4-octenoic acid (XI). Its synthesis as 6-pro-
propyl-2,3-dihydropyran-2,4-dione (XI) is reported by Kögl and Salemink 25.
The identity of PPD with the compound reported by these authors was con-
firmed by mixed m.p. determination of the synthetic 6-propyl-2,3-dihydrop-
pyran-2,4-dione. PPD was thus shown to be a homolog of triacetic lactone
(XII), the compound easily obtained from dehydroacetic acid (XIII) 24,26.

Phloropyron (X) was synthesised by dissolving 3-butyrylfilicinic acid (VIII)
and 6-propyl-2,3-dihydropyran-2,4-dione (XI) in dilute alkali and treating the
solution with formaldehyde. The m.p. of the synthetic phloropyron was 111—
112⁰ showing no depression on mixing with natural phloropyron. Desbuty-
rophloropyron, synthesised correspondingly from filicinic acid and 6-propyl-
2,3-dihydropyran-2,4-dione, was shown to have the structure (IX).

As already mentioned, propionic acid could be identified among the volatile
acids obtained by alkaline cleavage of phloropyron. This acid, however, could
not be found when 6-propyl-2,3-dihydropyran-2,4-dione was treated similarly.
Likewise, methyl ethyl ketone could be identified in phloropyron decomposi-

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tion but was lacking when 6-propyl-2,3-dihydropyran-2,4-dione was the starting material. These facts can be explained by the primary cleavage of phloropyron which yields both 6-propyl-2,3-dihydropyran-2,4-dione and 3-methyl-6-propyl-2,3-dihydropyran-2,4-dione, the latter producing the decomposition compounds mentioned.

There is every probability that the methylene bridge in the phloropyron molecule is attached to the carbon 3 of 6-propyl-2,3-dihydropyran-2,4-dione as shown in (X) leaving the carbon 5 as the less plausible one. To confirm this the condensation products of 6-propyl-2,3-dihydropyran-2,4-dione (XIV) and triacetate lactone (XV) with formaldehyde, called methylene-bis-compounds, were synthesised. Both were obtained in good yields by the method described before. This is in full agreement with earlier reports concerning methylene-bis-triacetic lactone condensed by slightly different methods, which confirms the position of the methylene bridge in (X).

The ultraviolet absorption curve of 6-propyl-2,3-dihydropyran-2,4-dione closely resembles that of triacetate lactone (Fig. 1) showing an abnormal hypsochromic shift in alkaline solution, $A_{\text{max}}^{\text{NaOH}}$ 277 $\mu$ (log $\varepsilon$ 3.89), which earlier has been observed in the case of 4-hydroxy-2-pyrones and their enol tautomers.

The ultraviolet absorption has been shown to differentiate between the 2- and 4-pyrone structures in the absence of additional chromophoric groups. From this it follows that 6-propyl-2,3-dihydropyran-2,4-dione exhibiting $A_{\text{max}}$ 283 $\mu$ (log $\varepsilon$ 3.88) and $A_{\text{min}}$ 242 $\mu$ (log $\varepsilon$ 3.28) clearly exists as a 2-pyrone tautomer in ethanol solution.

The infrared spectrum of 6-propyl-2,3-dihydropyran-2,4-dione (Fig. 2), however, considerably varies from that reported for triacetate lactone, for which a strong carbonyl absorption band at 1720 cm$^{-1}$ and further bands at about 1650 cm$^{-1}$ and 1250 cm$^{-1}$ indicate a typical 2-pyrone structure. 6-Propyl-2,3-dihydropyran-2,4-dione has no absorption band at 1720 cm$^{-1}$, the first carbonyl band occurring at 1677 cm$^{-1}$ which is close to the carbonyl absorption band reported for 4-pyrones ($1660 - 1670$ cm$^{-1}$) and therefore a 4-pyrone structure for this compound in the solid state appears to be the most probable one. 6-Phenyl-2,4-pyrone is reported to behave similarly.

To our knowledge the case of phloropyron is unique among the naturally occurring phloroglucinol derivatives, formulated as dimerous methylene compounds, since a phloroglucinol group is substituted by a pyronic group.

**EXPERIMENTAL**

The ultraviolet spectra were measured on a Unicam SP.500 instrument. The infrared recording was carried out in the Finnish Pulp and Paper Research Institute, Helsinki, using a Perkin-Elmer model 21 instrument fitted with a sodium chloride prism. The microanalyses were done partly in the laboratory of Dr. A. Bernhardt, Mühlheim, Germany and partly in the Department of Chemistry, University of Helsinki. The gas chromatographic analysis was done on a Perkin-Elmer model 154-B gas chromatography set in the Research Laboratories of the State Alcohol Monopoly, Helsinki.

*Isolation of phloropyron.* The finely ground rhizomes of *Dryopteris australis* (Jacc.) Wynn were extracted with ether for 8 hours. The solvent was distilled off and the resi-
due freed of fatty materials by MgO treatment. The "raw aspidin" so obtained was dissolved in ether and extracted with sodium carbonate (2 %) and this solution was reextracted with ether. The ether residue and the ethereal extracts were rejected. The sodium carbonate solution was acidified with dilute hydrochloric acid, the obtained precipitate filtered off, dried in vacuum and dissolved in methanol. The first substance which crystallised from methanol at 4 ° was flavaspic acid and was rejected. The following crystallisations contained phloropyron together with flavaspic acid and small amounts of desaspidin. Phloropyron was recrystallised from ethanol and light petroleum. The pure product had a m.p. of 111—112°. (Found: C 64.54; H 6.70. Calc. for C_{10}H_{14}O, C 64.60; H 6.67).

The aniline derivative of phloropyron. 10 g of phloropyron and 8 g of aniline, redistilled b.p. 184°, were mixed on a steam bath and 25 ml of absolute ethanol was added. The mixture was kept in the refrigerator for some days and the crystals filtered off. Recrystallisations from ethanol yielded white crystals, m.p. 111—112°. (Found: C 69.25; H 6.53; N 3.28. Calc. for C_{11}H_{15}ON C 69.67; H 6.66; N 3.01).

Phloropyron and its aniline derivative have widely different Rf-values, 0.28 and 0.95, respectively. Treated with dilute alkali the aniline derivative of phloropyron yielded unchanged phloropyron.

Alkaline cleavage of phloropyron. Phloropyron (300 mg) was dissolved in aqueous sodium hydroxide (2 M, 50 ml), zinc dust (600 mg) was added and the mixture boiled for 8 h. After addition of water (100 ml) the solution was acidified with sulphuric acid (10 %) and the volatile acids were distilled off and collected in a measured volume of standard alkali. The excess of alkali was determined by potentiometric titration. The amount of fatty acids, calculated as butyric acid, was about 45 % of phloropyron. For qualitative analysis of the fatty acids the titrated solution was made alkaline and evaporated to dryness. 5 ml of water was added and the solution made acidic with sodium hydroxide and extracted with n-butanol. The butanol solution was neutralised with ethyamine and the volatile acids chromatographed as their ethyamine salts.

Butyric acid and minor amounts of acetic acid and propionic acid could be identified.

The sulphuric acid solution was extracted with chloroform and filicinic acid (VII) was identified in the chloroform solution by paper chromatographic separation (Rf-value in n-butanol-acetic acid:water 5:1:4) was 0.83, which is identical with the Rf-value obtained for authentic filicinic acid, m.p. 215—220° (decomp.).

In the alkaline cleavage of phloropyron for obtaining butyrylfilicinic acid (VIII) as the degradation product, phloropyron was added to a boiling solution of sodium hydroxide (1 M) containing zinc dust. The mixture was boiled for 5 min and after cooling and filtering the solution was acidified with diluted sulphuric acid. Butyrylfilicinic acid was extracted with ether and identified in the ethereal residue by paper chromatography.

Acidic cleavage of phloropyron. Phloropyron (800 mg) was dissolved in conc. sulphuric acid (10 ml) and heated on a steam bath for 10 min. The mixture was diluted with 100 ml of water, cooled and the precipitate filtered off. The volatile acids were steam distilled

and determined as before. A yield of about 22% was obtained; by paper chromatographic analysis only butyric acid could be identified.

The precipitate was dried in vacuum and crystallised from benzene and aqueous ethanol (60%). M.p. 181—182°. (Found: C 63.76; H 6.37. Desbutyrophloropronyn (IX) \( \text{C}_7\text{H}_{10}\text{O}_4 \) requires C 63.75; H 6.25).

**Isolation of PPD.** Phloroprony was dissolved in sodium carbonate (2%) and boiled for some minutes. The cooled solution was made acidic with hydrochloric acid (10%) and kept at room temperature over night. The clear liquid was poured off and extracted with chloroform. The solvent was evaporated and the residue dissolved in water on a steam bath. The filtered solution was chromatographed through a column of perlum powder with water as an eluent. Use was made of the ferrie chloride reaction in fractionation and PPD was finally located by condensing an aliquot of each fraction with butyrylfileneic acid and formaldehyde in dilute alkali. Phloroprony thus obtained was identified by paper chromatography. PPD once isolated by this technique was subsequently prepared by omitting the peron chromatography step and instead continuing directly with the crystallisations from water and carbon tetrachloride. The pure product had a m.p. of 93—94°. (Found: C 62.33; H 6.67. Calc. for \( \text{C}_4\text{H}_{10}\text{O}_4 \) C 62.34; H 6.49).

**Hydrogenation.** PPD (1 mg) in ethanol solution was hydrogenated in a Warburg apparatus over palladised charcoal (10%) at 35°. The uptake, 1 mole of hydrogen, was completed in 3 h.

**Methoxylatlon of PPD.** PPD (50 mg) was methoxylated in ethereal solution with diazomethane. The obtained product was analysed without further purification. (Found: C 61.92; H 7.05; OCH\(_3\) 18.19. Calc. for \( \text{C}_4\text{H}_{11}\text{O}_4\text{N} \) C 64.25; H 7.14; OCH\(_3\), 18.45).

**Diazaoaminobenzene derivative of PPD.** To PPD (154 mg) dissolved in ethanol (5 ml) was added diazaoaminobenzene (197 mg) in ethanol (5 ml). The solution was heated on a steam bath for some minutes and then kept at room temperature overnight. The precipitate as recrystallised from ethanol had a m.p. of 134—135°. (Found: C 65.64; H 5.44; N 11.30. Calc. for \( \text{C}_4\text{H}_{11}\text{O}_4\text{N} \) C 65.12; H 5.42; N 10.85).

**Alkaline cleavage of PPD.** PPD was refluxed with sodium hydroxide (5%) for 2 h. After adding water the solution was distilled and the distillate treated with dinitrophenyl-hydrazine in hydrochloric acid (10%). Using paper chromatographic analysis of the dinitrophenylhydrazine mixture was separated by repeated recrystallisations into two main ketonic compounds: the one with acetone, m.p. 125—127° and the other with methyl propyl ketone, m.p. 145—146°. No depression was observed in mixed m.p. determinations with pure dinitrophenylhydrazones of acetone and methyl propyl ketone. (Found: C 45.49; H 4.42; N 23.8. The acetone derivative \( \text{C}_4\text{H}_{10}\text{O}_4\text{N} \) requires C 45.38; H 4.20; N 23.6. Found: C 49.74; H 5.30; N 22.1. The methyl propyl derivative \( \text{C}_4\text{H}_{11}\text{O}_4\text{N} \) requires C 49.62; H 5.25; N 21.05.)

The reaction product resulting from the alkaline cleavage was acidified with sulphuric acid and then steam distilled for volatile acids and the distillate was collected in sodium hydroxide. The salt solution was evaporated to dryness and the liberated acids were extracted with n-butanol. Paper chromatographic analysis indicated butyric acid and acetic acid. In order to distinguish between n-butyric and iso-butyric acids the salt mixture was evaporated and the acids liberated as before. Now the mixture was extracted with ether. The ethereal solution was gas chromatographed. Found: retention time 7.0. Authentic specimens of n-butyric acid, b.p. 163° and iso-butyric acid, b.p. 154° had retention times of 7.0 and 5.3, respectively.

**Acidic cleavage of PPD.** PPD was boiled with dilute sulphuric or phosphoric acid for one hour. The determination of the liberated carbon dioxide resulted in 1 mole CO\(_2\). In order to isolate heptane-2,4-dione, the acidic decomposition mixture was steam distilled and the distillate extracted with ether. The etheral extract was evaporated and the residue dissolved in methanol and treated with aqueous copper acetate. A greyish blue copper complex was obtained, m.p. 167—169°. (Found: C 52.97; H 6.94; Cu 19.9. Calc. for \( \text{C}_4\text{H}_{12}\text{O}_4\text{Cu} \) C 52.90; H 6.93; Cu 20.0.)

**Synthesis of heptane-2,4-dione.** Acetone was acylated with butyric acid ethyl ester by means of sodium amide yielding heptane-2,4-dione which was converted to its copper complex as described before. M.p. 168—169°, and mixed m.p. 167—169°. (Found: C 52.82; H 6.87; Cu 20.1. Calc. for \( \text{C}_4\text{H}_{12}\text{O}_4\text{Cu} \) C 52.90; H 6.93; Cu 20.0.) The copper contents were determined by a complexometric titration.

STRUCTURE OF PHLOROPYRON

Synthesis of 6-propyl-2,3-dihydropyran-2,4-dione (XI). According to Kögl and Salemkirn 26 PPD was prepared synthetically as follows: n-butyryl chloride and sodium enolate of acetyl acetic acid ethyl ester were condensed forming butyryl acetyl acetic acid ethyl ester. After splitting off the acetyl chain the resulting butyryl acetic acid ethyl ester was self-condensed giving butyryl PPD. This was converted to PPD by splitting off the butyryl group. The product obtained had a m.p. of 93—94°. Mixed m.p. with isolated PPD was 93—94°. (Found: C 62.28; H 6.46. Calc. for C₁₇H₂₉O₂: C 62.34; H 6.49)

Synthesis of phloropyron (X). Butyrilfelicinic acid (224 mg) and PPD (154 mg) were dissolved in potassium hydroxide (10 ml, 1%) and formaldehyde (0.75 ml, 4%) was added. The mixture was kept at room temperature for 15 min and made acidic with hydrochloric acid (10%). The precipitate was filtered off, washed with water and dried. After several recrystallisations from ethanol the product had a m.p. of 111—112° and with natural phloropyron a mixed m.p. of 111—112°. (Found: C 64.92; H 6.74. Calc. for C₁₄H₂₀O₄: C 64.60; H 6.67.)

Synthesis of desbutyrophloropyron (IX). Folicinic acid (154 mg) and PPD (154 mg) were dissolved in potassium hydroxide (10 ml, 1%) and formaldehyde (0.75 ml, 4%) was added. The mixture was kept at room temperature for 15 min and made acidic with hydrochloric acid (10%). The precipitate was filtered off, washed with water and dried. The identification was made by paper chromatographic analysis 11. The Rf-value was identical with that of desbutyrophloropyron, m.p. 161—162°, obtained by acidic cleavage of isolated phloropyron.

Synthesis of methylene-bis-PPD (XIV). PPD (308 mg) was dissolved in potassium hydroxide (20 ml, 1%) and formaldehyde (0.75 ml, 4%) was added. The mixture was kept at room temperature for 24 h and acidified with hydrochloric acid (10%). The precipitate was collected, washed with water and dried in vacuum. Recrystallisation from light petroleum yielded a product with a m.p. of 67—69°. (Found: C 64.09; H 6.34. Calc. for C₁₇H₂₉O₄: C 63.75; H 6.25.)

Synthesis of methylene-bis-triaacetic lactone (XV). Triacetic lactone, m.p. 188—189°, was prepared from dehydroacetic acid, m.p. 110—112°, by the method of Collie 25.

Triacetic lactone (2.52 g) was dissolved in potassium hydroxide (200 ml, 1%) and treated with formaldehyde (0.75 ml, 40%). After standing at room temperature for 15 min the solution was acidified and the product recrystallised from ethanol, m.p. 250—251°. (Found: C 59.19; H 4.54. Calc. for C₁₇H₂₉O₄: C 59.07; H 4.58.)

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