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THE STRUCTURE OF PERIPLANETIN*

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Abstract—The crystalline substance, $C_{13}H_{16}O_7$ periplanetin, isolated from the secretion of the laterocervical organ of *Periplaneta americana* L. and *Blatta orientalis* L., is *1-benzoyl-β-D-glucose*, (II) whose occurrence in nature has not hitherto been reported.

As previously reported,[1] the solid secretion of the laterocervical organ of some Blattidae (*Periplaneta americana L., Blatta orientalis L.*) contains a crystalline white substance designated *periplanetin*. From 1000 insects (males and females) of *P. americana* weighing 880 g, 40–50 mg of the pure product can be isolated.

Periplanetin crystallises from water in small white prisms, melts undecomposed at 193°, is neutral and shows a blue-whitish fluorescence at the Wood's light. Its molecular formula is $C_{13}H_{16}O_7$. Because of the difficulty in obtaining starting material, which is isolated from fresh insects by a tedious process, a study of the infra-red spectrum of the pure substance was undertaken before any chemical investigation.

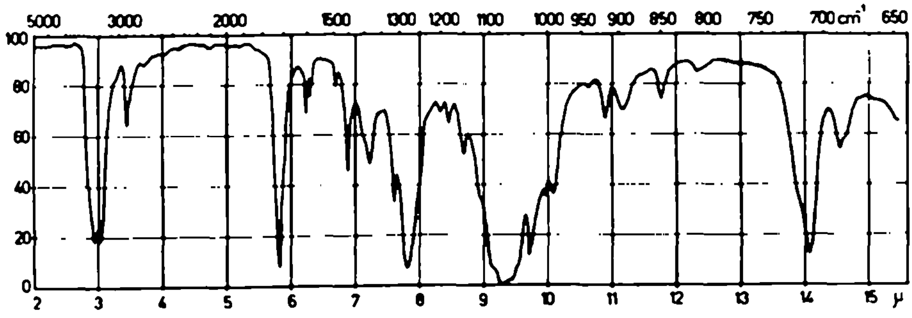

FIG. 1. I.R. spectrum of periplanetin (in KBr).

The *infra-red spectrum* of periplanetin in KBr (Fig. 1) shows in the 3500–3200 cm^{-1} region a strong and complex band assignable to OH groups and this is supported by the presence of a broad band at 1100–1050 cm^{-1}. The existence of a limited number of CH_2 groups is suggested by the occurrence of the bands at 2920, 2860 and 1450 cm^{-1}, whereas the lack of absorption in the 2960 cm^{-1} region indicates that CH_3 groups are not present. The existence in periplanetin of aromatic nuclei is clearly demonstrated by a number of characteristic absorptions; such as the three bands in the 1600–1500 cm^{-1} region, the intense band at 710 cm^{-1}, and some weak bands in the 1250–950 cm^{-1} region. Moreover, the intensity of the doublet at 1604 and 1585 cm^{-1} suggests a conjugation of the benzene ring with other unsaturated groups. There are two strong

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[1] M. Pavan, *Boll. Soc. Ital. Biol. Sperim.* **30**, 873, 875 (1954).

bands at 1715 and 1279 cm^{-1}; the first, on account of its position and intensity, may be assigned to the C=O and the second to the C—O stretching vibration of an aromatic ester, confirmed by the intense band at 1100 cm^{-1} which appears on the side of the broad band due to the alcoholic C—O.

From the above data and a comparison of the frequencies of the characteristic bands in i.r. spectra of periplanetin and some benzoic esters (Table 1),[2] it may be safely concluded that periplanetin is the benzoate of a polyhydroxylated compound which still contains free OH groups in its molecule.

TABLE 1. FREQUENCIES (cm^{-1}) OF THE CHARACTERISTIC BANDS IN I.R. SPECTRA OF PERIPLANETIN AND SOME BENZOATES

Compound	C=O	Aromatic ring			C—O		Aromatic CH
Methyl benzoate	1725	1607	1585	1496	1277	1108	707
Ethyl benzoate	1725	1608	1588	1497	1277	1108	709
iso-Propyl benzoate	1715	1608	1588	1492	1274	1108	708
iso-Pentyl benzoate	1725	1609	1590	1496	1274	1111	708
Periplanetin	1715	1604	1585	1493	1279	1100	710

Taking into account its molecular formula, periplanetin must, therefore be a *mono-benzoyl-hexose*, $C_6H_5CO{-}OC_6H_{11}O_5$. Accordingly, on short heating with 12% HCl on the water-bath, periplanetin affords a crystalline acid m.p. 121° which is identical with *benzoic acid*. The aqueous solution, evaporated *in vacuo* at ordinary temperature after removal of benzoic acid, leaves a glassy residue which readily reduces Fehling's solution.

Owing to the difficulty of obtaining a crystalline product from the small quantity of substance available, the identification of the sugar moiety in periplanetin was performed by paper chromatography. The experiments summarised in Table 2 indicate that the hexose formed from the hydrolysis of periplanetin is D-*glucose*.

Periplanetin is, therefore, a *benzoyl*-D-*glucose* in which configuration and position of the benzoyl group is still to be confirmed. Since benzoic acid is formed on treatment

TABLE 2. PAPER CHROMATOGRAPHY OF THE SUGAR FROM PERIPLANETIN AND OF NATURAL HEXOSES

Hexose	Eluent butanol-pyridine-water 6:4:3 R_f	Eluent butanol-acetic acid-water 4:1:5 R_f	Eluent ethyl acetate-pyridine-water 10:4:3 R_f
D-Galactose	0·34	0·20	0·46
D-Glucose	0·38	0·20	0·52
Sugar from periplanetin	0·38	0·20	0·52
D-Fructose	0·42	0·23	0·59
D-Mannose	0·43	0·23	0·57

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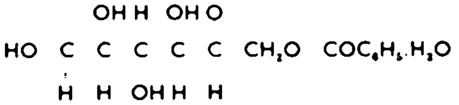
[2] *D.M.S. Spectral Cards* No. 1043, 1241, 1044 and 1045.

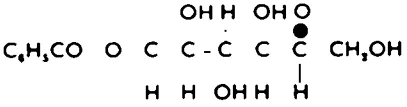
of the substance with *emulsin* in the presence of calcium carbonate, periplanetin is most probably a *β-glucoside*.

Only two D-glucose *mono*benzoylderivatives have been reported in the literature, namely, *6-benzoyl-D-glucose* or *vacciniin* (I), originally isolated from the juice of the bearberry (*Vaccinium vitis idea.* L.)[3] and synthesised by Fischer and North;[4] *1-benzoyl-β-D-glucose* prepared by Zervas[5] but not found in nature. Periplanetin is not vacciniin (which contains a molecule of water and melts at 104-106°), but could be identical with Zervas' 1-benzoyl-β-D-glucose, which also melts at 193° and does not form a hydrate. Further, *tetraacetylperiplanetin* m.p. 140°-141° may be identical with 1-benzoyl-β-D-glucose tetraacetate,[5] m.p. 145°.



$$HO\,\underset{H}{C}\,\underset{H}{\overset{OH}{C}}\,\underset{OH}{\overset{H}{C}}\,\underset{H}{\overset{OH}{C}}\,\underset{H}{\overset{O}{C}}\,CH_2O\,COC_6H_5.H_2O$$

I. Vacciniin



$$C_6H_5CO\,O\,\underset{H}{C}\,\underset{H}{\overset{OH}{C}}-\underset{OH}{\overset{H}{C}}\,\underset{H}{\overset{OH}{C}}\,\underset{H}{\overset{O}{C}}\,CH_2OH$$

II. Periplanetin

That periplanetin is actually 1-benzoyl-β-D-glucose has been proved by synthesis[5] (benzoylation of 4:6-benzylidene-α-D-glucose followed by catalytic hydrogenolysis of the benzylidene derivative). Synthetic periplanetin melts at 191° undecomposed and the m.p. is not depressed on mixing with the natural product. The *infra-red spectra* of natural periplanetin and synthetic 1-benzoyl-β-D-glucose as well as those of the corresponding tetraacetates reported in Fig. 2, also confirm the identity of the two substances.

Although the occurrence of aromatic 1-esters of D-glucose in plants had been reported,* no example was known of the isolation of substances of this type from animal organisms. The function of periplanetin in the insect's economy is still unknow but it seems possible that it may represent the form in which benzoic acid is excreted from the organism.

EXPERIMENTAL

Extraction and purification of periplanetin. The crude product was obtained by scraping the material deposited on the surface of the insect's neck and by removing the gland by which the substance is secreted.† From about 3000 insects of *Periplaneta americana* L., 0·462 g of material were collected. The coarse grey powder thus obtained, which contains mechanical impurities (hairs, fragments of cuticle etc.) was suspended in 20 ml of water at 35°–40°, filtered and the clear solution, after extraction with peroxide-free ether, was decolorised with Norit. From the ethereal layer 55 mg of a crystalline acid m.p. 120-121° identical with benzoic acid were obtained.

The aqueous solution, dried *in vacuo* over P_2O_5 and KOH, gave 230 mg of a white crystalline residue which was purified by repeated recrystallisation from water. In total 150 mg of fairly pure periplanetin were isolated. In the mother liquors some free sugar was present (aniline phtalate test).

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* Glucogallin, found in Chinese rhubarb, is 1-galloyl-β-D-glucose. See: E. Gilson, *Bull. Acad. Roy. Méd. Belg.* 4, 16, 837, 842, 851 (1902); E. Fischer and M. Bergmann, *Ber. Dtsch. Chem. Ges.* 51, 1766 (1918).

† The location of the product is rendered evident by the intense blue-whitish fluorescence at the Wood's light.

[3] C. Griebel, *Chem. Zentr.* I, 540 (1910).

[4] E. Fischer and H. Noth, *Chem. Zentr.* I, 488 1917; *Ber. Dtsch. Chem. Ges.* 51, 326, 330 (1918).

[5] L. Zervas, *Ber. Dtsch. Chem. Ges.* 64, 2289 (1931).

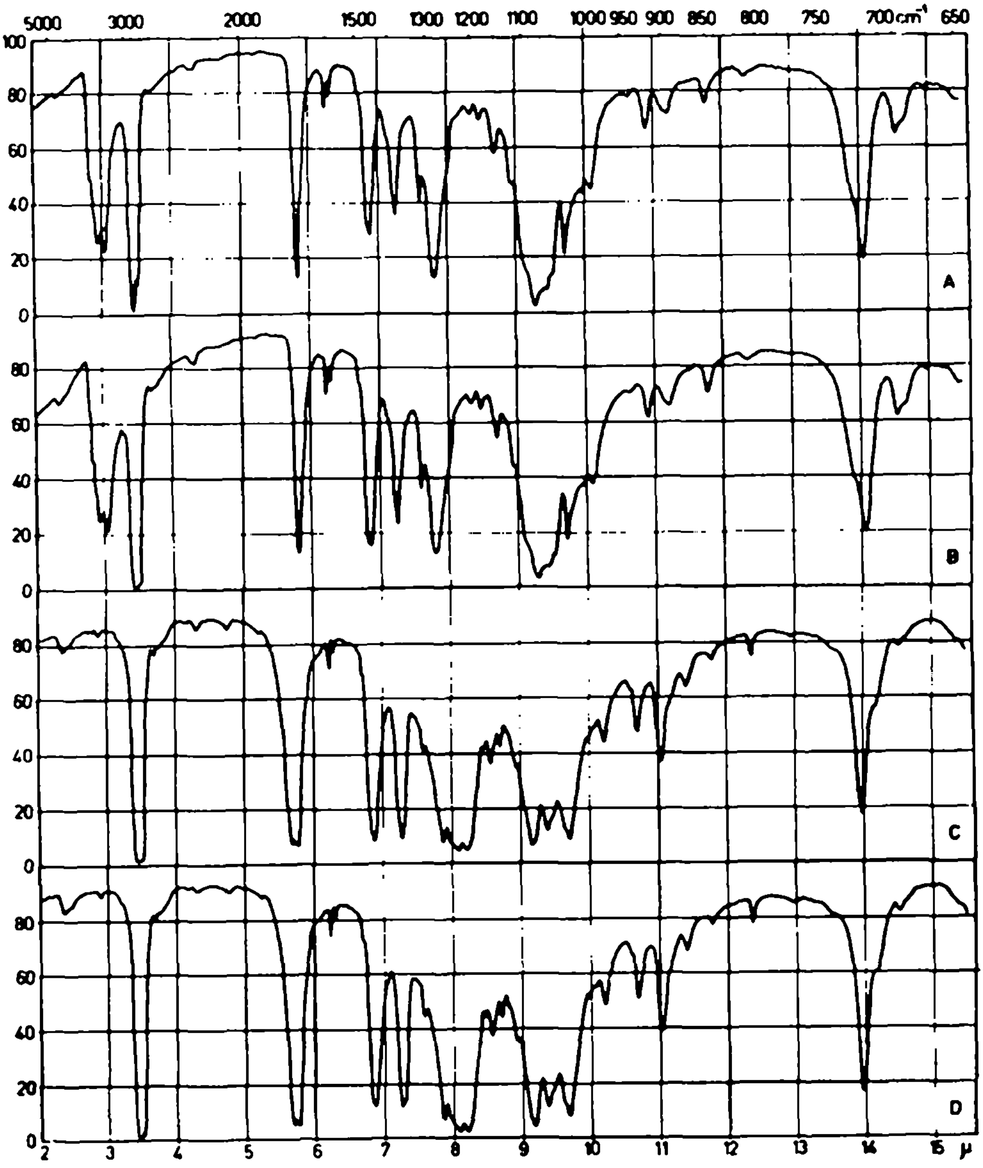

FIG. 2. I.R. spectra in Nujol.
A—Natural periplanetin
B—Synthetic 1-benzoyl-β-D-glucose
C—Tetraacetylperiplanetin
D—Tetraacetyl-1-benzoyl-β-D-glucose

Pure periplanetin forms small silver-white prisms m.p. 193°. It is readily soluble in water, ethanol and methanol, and shows a characteristic blue-white fluorescence at the Wood's light. The i.r. spectrum (in KBr) is reported in Fig. 1. (Found: C, 54·99; H, 6·07. Calc. for $C_{13}H_{16}O_7$: C, 54·93; H, 5·67%).

The product isolated from *Blatta orientalis L.* by the same procedure melted at 193° and possessed an i.r. spectrum identical to that of periplanetin.

Hydrolysis of periplanetin with acids. A solution of periplanetin (50 mg) in HCl (12%, 15 ml) was heated for 5 min on the water-bath, and then evaporated to dryness *in vacuo* at room temperature over P_2O_5 and KOH. The solid residue was dissolved in water and the solution shaken with peroxide-free ether. The ethereal layer on evaporation gave benzoic acid (13 mg) which melted, after sublimation, at 121°. The aqueous solution, treated with Norit and evaporated over P_2O_5 and KOH *in vacuo*, yielded a glassy residue containing the sugar moiety of periplanetin.

The identification of the sugar was performed by paper chromatography (N.1 Whatman paper) using as solvents the mixtures: *n*-butanol-pyridine-water 6:4:3;[6] *n*-butanol-acetic acid-water 4:1:5[7]; ethyl acetate-pyridine-water 10:4:3.[8] After spraying with aniline phthalate solution[9] (*n*-butanol saturated with water 50 ml, phthalic acid 0·83 g, aniline 0·46 g) and heating at 105° for 10 min brown spots which show a yellow-greenish fluorescence at the Wood's light are developed. The values of the R_f reported in Table 2 demonstrate that the sugar formed by hydrolysis of periplanetin is D-glucose.[2]

Enzymatic hydrolysis of periplanetin. Periplanetin (30 mg) dissolved in water, (10 ml) commercial emulsin (Fluka), 80 mg and precipitated $CaCO_3$ (120 mg) were added. After 24 hr at room temperature the mixture was treated with dilute HCl and extracted with ether. The ether layer evaporated gave *benzoic acid* m.p. 120°. In an experiment under the same conditions but in absence of emulsin, no benzoic acid was formed.

Tetraacetylperiplanetin. To a mixture of acetic anhydride (80 mg) and pyridine (60 mg) periplanetin (30 mg) was added. Solution was complete in about 2 hr. After 24 hr at room temperature the crystalline mass was poured into water (2 ml) and the precipitate filtered. After repeated crystallisation from ethanol tetraacetylperiplanetin forms white needles m.p. 140–141°. The i.r. spectrum (Nujol) is shown in Fig. 2, C. (Found: C, 55·10; H, 5·75. Calc. for $C_{21}H_{24}O_{11}$: C, 55·75; H, 5·35%).

Synthetic periplanetin. 1-Benzoyl-β-D-glucose was prepared according to Zervas[5] but it was found that the hydrogenolysis of 1-benzoyl-4:6-D-glucose proceeds better in acetic acid solution than in methanol as suggested by that author. The product, obtained by removal of the solvent *in vacuo* at room temperature and purified by repeated crystallisation from water, formed white prisms m.p. 191°. The mixture with authentic periplanetin melted at 190°. The i.r. spectrum (Nujol) of synthetic periplanetin reported in Fig. 2, B, is identical with that (Fig. 2, A) of the natural product.

Tetraacetyl-1-benzoyl-β-D-glucose, prepared from synthetic periplanetin as above and recrystallised from ethanol, melted at 139–140° and gave no depression mixed with tetraacetylperiplanetin m.p. 140–141°. The i.r. spectrum (Nujol) reported in Fig. 2 D, confirms the identity of the two products.

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[6] A. Jeanes, C. S. Wise and R. J. Dimler, *Analyt. Chem.* **23**, 415 (1951).

[7] S. M. Partridge, *Biochem. J.* **42**, 238 (1948).

[8] N. B. Chanda, E. L. Hirst and D. J. Manners, *J. Chem. Soc.* 1957, 1954.

[9] S. M. Partridge, *Nature, Lond.* **164**, 443 (1949).