LXI.—On *Phlorizin*.

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IN a paper on "Glycyphyllin, the Sweet Principle of *Smilax Glycyphylla*," communicated to the Society some few months ago (*Trans.*, 1886, 857), it was suggested as possible, though scarcely probable, that this substance might be identical with phlorizin. The idea of such a possibility arose out of the following considerations:—

1. Glycyphyllin yields phloretin and isodulcite on hydrolysis, whereas phlorizin yields phloretin and a sugar about which some uncertainty has hitherto existed; Hesse maintaining (*Miller's Chemistry*, 5th Edition, Part III, 582) for reasons to be hereafter mentioned, that it is *not* identical with ordinary dextrose. Moreover, isodulcite has apparently been more than once mistaken for dextrose. (See Will, *Ber.*, **18**, 1312.)

2. Considerable discrepancies are noticeable in the published analysis of phlorizin, so much so that the generally accepted formula of Stas, $C_{21}H_{24}O_{10}$, has been called in question by Loewe (*Watts' Dictionary*, **8**, Part II, p. 1569), who proposes another formula and another equation to represent its hydrolysis. His results, however, as is pointed out (*loc. cit.*), do not harmonise well with known

facts. Hugo Schiff also (*Ber.*, **14**, 303) has drawn attention to the want of agreement in the published analyses of phlorizin.

Under these circumstances, it seemed worth while to re-examine this substance, and to that end a specimen obtained from Trommsdorff was twice recrystallised and then analysed.

Results of Analysis.

The following are the results in brief of four analyses of the anhydrous substance:—

	Theory for $C_{21}H_{24}O_{10}$.	Found.			
		I.	II.	III.	IV.
Carbon ..	57.79	57.03	57.11	57.15	57.17
Hydrogen.	5.50	5.89	5.91	5.67	5.70
Oxygen ..	36.71	—	—	—	—
	<hr/> 100.00				

Though these numbers are not very far from those indicated by theory for the above formula, they are scarcely satisfactory. A fresh specimen was therefore prepared by repeated crystallisation from water. The substance so obtained consisted of perfectly white, well-defined, silky needles; it was analysed without dehydration, having been previously thoroughly air-dried. It contained 7.58 per cent. of water of crystallisation, the theory for 2 mols. H_2O requiring 7.62 per cent. The following are the results:—

	Substance.	CO_2 .	H_2O .
I	0.3202	0.6217	0.1792
II	0.3109	0.6065	0.1728

	Calculated for $C_{21}H_{24}O_{10} \cdot 2H_2O$.		I.	II.
	252	53.39		
C_{21}	28	5.93	52.95	53.20
H_{28}	192	40.68	6.21	6.17
O_{12}	<hr/> 472	<hr/> 100.00	—	—

These number are much more satisfactory and confirm the original analyses and formula of Stas.

Decomposition by Dilute Sulphuric Acid.

It being impossible to refer to the original papers here in Adelaide, it has not been possible to ascertain whether any quantitative experi-

ments have been made to determine the amounts of phloretin and sugar, respectively, yielded by the hydrolysis of phlorizin. Two experiments were therefore made, the method used being practically the same as that described in the case of glycyphyllin (*Trans.*, 1886, 864), except that the main portion of the phloretin was weighed on a filter-paper of known weight. The results of the titration of the filtrate were of course calculated on the assumption that the sugar is dextrose.

The following were the numbers obtained :—

Anhydrous substance.	Phloretin.	Dextrose.	
2.2980	1.4375	0.9671	
3.3114	2.0729	1.3514	
Calculated for hitherto assumed equation.		Found.	
		I.	II.
Phloretin	62.82 per cent.	62.55	62.59
Dextrose	41.28 „	42.09	40.80

These numbers are sufficiently near to those required by the hitherto assumed equation—

to afford strong confirmation of its truth. It may be noted here that the equation by which Loewe (*Watts' Dictionary*, 8, Part II, p. 1570) represents the decomposition of phlorizin, requires 63.5 per cent. phloretin and only 36.4 per cent. dextrose, reckoned on the anhydrous substance.

Examination of the Sugar obtained.

The filtrate from the decomposition (by dilute sulphuric acid) of a considerable quantity of phlorizin was neutralised by barium carbonate, filtered and concentrated over a water-bath. A good deal of colouring matter formed. This was removed by repeated treatment with animal charcoal, and the solution finally concentrated to a syrup in a vacuum, over sulphuric acid. On adding a small quantity of water to this syrup, and allowing it to stand for a few days exposed to the air, it gradually became an almost solid mass of minute, perfectly white crystals. These were dried on the filter-pump, washed two or three times with a small quantity of water, and finally spread out to dry in the air.

According to Hesse (*Miller's Chemistry*, 5th Edition, Part III, p. 582) the sugar from phlorizin differs from dextrose in the following particulars :—

1. The melting point of the hydrated crystals is 74° , that of dextrose being 82° according to Hesse (*Annalen*, **176**, 103), or 86° according to Schmidt (*Annalen*, **119**, 92).

2. It loses only 6.7 per cent. of water at 60 — 70° , and requires a temperature of 105° to expel the last traces of water.

3. The specific rotatory power (sodium light) after standing, is 44° , that of dextrose according to various observations ranging from about 53° to 57.6° for solutions containing 10 per cent., or thereabouts, of anhydrous glucose.

With reference to the second point, there seems to be some difference of opinion as to the temperature at which dextrose becomes anhydrous. In the latest edition of Beilstein's *Handbuch der organischen Chemie* is the following statement: "Krystallisirter Traubenzucker verliert das Krystallwasser unter 100° unter Schmelzung und ist bei 110° wasserfrei," apparently implying that a temperature of 110° is required to remove the last traces of water.

The sugar under examination melted at 85 — 86° when carefully heated in a capillary tube. Heated at 100° , it lost 8.64 per cent. of its water: theory for 1 mol. H_2O indicating 9.09 per cent. Heated at 102 — 103° , the loss increased to 9.32 per cent.

A solution was made containing 10.204 grams anhydrous substance in 100 c.c.* This, after standing, gave a rotation of 11.83° in a tube 200 mm. in length, the observations being made with a Laurent's polarimeter using sodium light. This gives—

$$[\alpha]_D = \frac{11.83^{\circ}}{2 \times 0.10204} = 57.9^{\circ}.$$

Finally, a solution, when treated with phenylhydrazine hydrochloride in the manner recommended by Fischer (*Ber.*, **17**, 579), yielded a yellow, crystalline precipitate exactly corresponding with that described as given by dextrose, and with a melting point 204 — 205° , when heated in a capillary tube. The facts above adduced leave little doubt that the statements generally made as to the formula and hydrolysis of phlorizin are correct, and that the sugar yielded by it is really dextrose.

* It was intended to make this solution by dissolving a weighed quantity of the crystals in 100 c.c. water, but an accident having happened to the solution in course of preparation, and no more substance being available, the strength was carefully determined (after dilution) by titration with Fehling's solution.